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1. Introduction

The subject of this paper is related to the first-order magnetic phase transitions. The expression, first-order phase transition is used in its usual thermodynamical sense, i.e. the first derivatives of the system's Gibbs free-energy with intensive parameters /temperature, pressure, magnetic field, e.g./ exhibit a discontinuity at the critical values of these parameters. In other words, the molar entropy, molar volume, molar magnetization, and other molar parameters suffer discontinuous change. In the higher-order phase transitions the molar parameters are continuous but their derivatives are discontinuous. It is worthwhile to note here that the most characteristic feature of the higher-order phase transformations is the discontinuous change in symmetry of the system with the continuous change of the state of system. This approach was very successfully developed many years ago by Landau and Lifshitz [1] .

In order to systematize in a very simple way the magnetic phase transformations a "family tree" has been con-

structed from different types of transitions. This "family tree" is shown in Fig. 1. Some magnetic systems that exhibit transitions of first-order are listed in Table I. It is clear that the simplest case is when the crystal structure does not change during the magnetic structure transition and this latter takes place between ordered magnetic phases. Substantial theoretical difficulties being associated with those phase transformations where the magnetic order disappears they will be excluded from our considerations.

It is known already since the last century that the onset of the magnetic order /e.g. ferromagnetism/ results in a smaller or larger distortion of the crystal lattice /in many cases without any crystal symmetry change/. This phenomenon is related to the dependence of the exchange-energy on the interatomic spacing.

As a result of this dependence the free-energy of the crystal may be lowered by a distortion of the lattice in direction of decreasing exchange-energy. The distortion will introduce to the free-energy a term in strain energy which will increase the free-energy, and thus, a compromise between distortion and exchange is reached, which minimizes the free-energy. In the case of order-disorder phase transformations /i.e. ferromagnetic $\rightleftarrows$ paramagnetic, antiferromagnetic $\rightleftarrows$ paramagnetic/ the magneto-elastic coupling between the magnetic and elastic part of the systems's free-energy may drastically alter the character of phase transi-

tions. If the exchange parameter dependence on the interatomic spacing is rather strong a first-order phase transition will be observed instead of the usual second-order one.

The reason for this is quite obvious. The elastic distortion tends to stabilize the magnetic order, and thus, slows down its decrease with temperature. At a certain temperature, however, the magnetic order can find no way for decreasing smoothly to zero since the stabilizing influence of the lattice distortion ceases to act below a certain magnetic order, i.e. at a critical temperature the magnetic order and lattice distortion go to zero discontinuously. Using Bean's formulation [2] the situation is like that of a man who has run beyond the brink of a cliff; there is no gentle way down.

Of course, not only the appearance and disappearance of the magnetic order but in many cases the structure changes in the ordered phase may also lead to a remarkable variation of the crystal distortion. In the following these structure changes will be discussed and the aim of this paper is to give an elementary introduction to the physics of these phenomena.

2. Magnetic Structures and the Model

First of all, we have to discuss the conditions for the existence of various magnetic structures in a given

crystal lattice since our goal is to study the phase transitions between these structures. To do this in general is a very complex task and therefore we have to limit our considerations to the simplest case which is probably distinct from any real situation but has a great advantage, the possibility of an elementary treatment without incurring any substantial losses in the physically important conclusions.

The stability conditions required for a given magnetic structure can be derived when we first answer the following question: what are the possible magnetic structures in a given crystallographic symmetry ?

Assuming second-order character of the formation of various magnetic structures from the magnetic disorder /i.e. from the paramagnetic phase/ this question can be answered in principle very rigorously.

One have to notice here that the assumption of the second-order character of the magnetic structure formation does not mean any serious restriction on the character of the phase transitions between the ordered structures. Therefore, we could start our considerations in this way.

Unfortunately, answering the first question the problem of finding the criteria for the existence of various magnetic structures in terms of physical parameters remains still unsolved. If we want to solve this problem too, we need a more or less definite model containing important inform-

ations about the exchange interactions in the crystal.

We don't want to go into the details of the method with the help of which we can answer the first question; we refer only to some basic works in this field. Originally Landau and Lifshitz [1] proposed this theory for the investigations of the ordered structures in alloys. Later Dzyaloshinsky [3] and Kovalyov [4] applied it to the case of magnetic phase transformations and very recently a further generalization was made by Sólyom [5] .

This rigorous method can be used only for finding the possible magnetic structures but for the actual calculation we need always a definite model. Now we want to choose the simplest one which is still useful enough to illustrate the most important qualitative properties of the phase transformations.

In the following we will proceed from an improved version of the model proposed by Anderson [6] and Smart [7] . First of all, we choose a simple cubic lattice for the calculations and assume the exchange interaction between the localized magnetic moments to be different from zero only for the nearest and for the next-nearest neighbours. In order to ensure that within a given distance each lattice point should be surrounded by lattice points belonging to different sublattices one has to introduce a specified number of different sublattices only. If this

characteristic distance is the interatomic spacing between the next-nearest neighbour atoms, eight sublattices are required. The lattice points with their sublattice number are shown in Fig. 2.

Denote by $\bar{M}_j$ /j=1,...8/ the thermal averged magnetic moment in the j'th sublattice and write down the internal energy of the crystal per unit volume in molecular field approximation. We get

$$U_m = - \sum_{i,j} \bar{M}_i A_{ij} \bar{M}_j \qquad /2.1/$$

where

$$\tilde{A} = \begin{pmatrix} \tilde{A}_1 & \tilde{A}_2 \\ \tilde{A}_2 & \tilde{A}_1 \end{pmatrix} \qquad /2.2/$$

is the interaction matrix and

$$\tilde{A}_1 = \begin{pmatrix} 0 & a & b & a \\ a & 0 & a & b \\ b & a & 0 & a \\ a & b & a & 0 \end{pmatrix} \quad \tilde{A}_2 = \begin{pmatrix} b & a & b & 0 \\ 0 & b & a & b \\ b & 0 & b & a \\ a & b & 0 & b \end{pmatrix} \qquad /2.3/$$

Here we used the notations

$$a = \frac{1}{4} NJ_1 \quad , \quad b = \frac{1}{2} NJ_2 . \qquad /2.4/$$

J_1 and J_2 are the effective exchange parameters between the nearest and the next-nearest neighbours, respectively, and N is the number of atoms in the unit volume.

Taking into account that the effective internal field

$$\bar{H}_j = - \frac{\partial U_m}{\partial \bar{M}_j} \qquad /2.5/$$

$$/j=1,2,\ldots,8/$$

must have the same direction as the corresponding sublattice magnetization, i.e.

$$\bar{H}_j = \lambda \bar{M}_j \qquad /2.6/$$

we may get immediately the possible magnetic structures from the eigen-value equation

$$\left(A - \lambda \tilde{E}\right) \tilde{\bar{M}} = 0 \qquad /2.7/$$

where $\tilde{E}$ is the unit matrix and

$$\tilde{\bar{M}} = \begin{pmatrix} \bar{M}_1 \\ \bar{M}_2 \\ \vdots \\ \bar{M}_8 \end{pmatrix} \qquad /2.8/$$

is the structure matrix. One has to note that the independence of the proportionality factor λ of sublattice magnetization is valid only near the ordering temperature.

Making use of some theorems for block-matrices the eigen-values of the equation /2.7/ easily can be calculated. One finds

$$\lambda_1 = 3(a+b) \ , \quad \lambda_2 = -3(a-b) \ , \quad \lambda_3 = \lambda_4 = \lambda_5 = -(a+b)$$

$$\lambda_6 = \lambda_7 = \lambda_8 = (a-b) \ .$$

The magnetic structures are determined by the corresponding eigen-vectors belonging to these eigen-values. Results of the calculations are summarized in Table II. As one can see one ferromagnetic and three antiferromagnetic structures are possible in the frame of this very simple model. The anti-ferromagnetic unit cells are doubled in all three directions while the ferromagnetic one is identical with the chemical unit cell.

The eigen-value of a given structure is proportional to the ordering temperature. Between two phases it is the more stable which has a higher ordering temperature. The phase boundaries between the different phases are shown in Fig.3.

Four structure changes are possible, namely

F $\rightleftarrows$ AFI,	if $J_2 > 0$	and	J_1	changes its sign,
AFI $\rightleftarrows$ AFII,	if $J_1 < 0$	and	$4J_2-J_1$	" " "
AFII $\rightleftarrows$ AFIII,	if $J_2 < 0$	and	J_1	" " "
AFIII $\rightleftarrows$ F ,	if $J_1 > 0$	and	$4J_2+J_1$	" " "

A simple phenomenological description of the structure changes can be done in the following way. One finds that during the transition certain antiferromagnetically oriented pairs transform to ferromagnetic one and vice versa. Let 2Θ be the angle between the moments of transforming pairs in an intermediate /non-equilibrium/ state and denote by m the cosine of Θ i.e.

$$m = \cos\Theta \ . \qquad /2.9/$$

The magnetic part of the internal energy may be written as

$$U_m = - (A+\gamma B) M_o^2 \sigma^2 - B M_o^2 \sigma^2 (2m^2-1) \ , \qquad /2.10/$$

$$(A > 0)$$

where the parameter B which is an appropriate combination of interaction constants changes its sign during the phase transition. σ is the average relative magnetization per atom at temperature T, i.e.

$$\sigma = \frac{M}{M_o}$$

where M_o is atomic magnetic moment at $T = 0$. The values of A, B and γ for different structure changes are listed in Table III.

When the sign of the parameter B is changing the m has to vary from $m = 0$ to $m = 1$, or vice versa; in other words phase transformation takes place. It is important to

note that physical meaning can be attributed to m only in the case of antiferromagnetic ⇄ ferromagnetic transitions. In this case the meaning is evident; m is a measure of the bending between the moments.

It is absolutely clear that this oversimplified model can't give practically useful results but as we shall see later, a lot of physically interesting qualitative conclusions can be drawn from it.

The next step in perfecting the model is exploiting the sensitivity of the exchange parameters against the lattice distortions. First Néel [8] and later Smart [7], Bean and Rodbell [2], Kittel [9] and many others [10] emphasized the importance of this sensitivity and investigated its influence on the temperature behaviour of the magnetization. Now, we should like to apply some of their results in the theory of magnetic structure transitions which are associated with lattice distortions.

Let l_c be the distance between the nearest neighbour atoms at which the parameter B changes its sign. So, one may expand A and B into a power series of $l - l_c$. For sake of simplicity the terms higher than linear are neglected, i.e.

$$A = A_o + \left(\frac{d\,A(l)}{dl} \right)_{l=l_c} (l-l_c) ,$$

$$B = \left(\frac{d\,B(l)}{dl} \right)_{l=l_c} (l-l_c) . \qquad /2.11/$$

As it was already mentioned, the dependence of exchange interactions on the interatomic spacing leads to a spontaneous distortion of the lattice. The competition between the bonding and exchange forces will determine the actual value of the distortion. Let l_o be the distance between the nearest neighbour atoms at temperature $T=0$ in the absence of distortion and let ε be the relative dilation at temperature $T \geq 0$.

One get from /2.11/

$$A = A_o + A_1 (\varepsilon - \varepsilon_c) \quad \text{and} \quad B = B_1 (\varepsilon - \varepsilon_c) \qquad /2.12/$$

where

$$A_1 = \frac{1}{3} l_o \left(\frac{d A(l)}{dl} \right)_{l=l_c} \qquad /2.13/$$

and

$$B_1 = \frac{1}{3} l_o \left(\frac{d B(l)}{dl} \right)_{l=l_c} , \qquad /2.14/$$

while

$$\varepsilon_c = 3 \frac{l_c - l_o}{l_o} . \qquad /2.15/$$

In the presence of lattice distortion one has to add to the internal energy an elastic energy term which in its simplest form is

$$U_e = \frac{1}{2} R \varepsilon^2 , \qquad /2.16/$$

where

$$\frac{1}{R} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad /2.17/$$

is the compressibility.

The thermodynamics of the phase transition can be founded on the Gibbs free-energy per unit volume. Denoting by S_m and S_l the magnetic and the lattice entropy we can write

$$G = U_m + U_e + P\varepsilon - T\left(S_m + S_l\right) . \qquad /2.18/$$

This is the appropriate form of the free-energy needed in our case. In accordance with the molecular-field approximation the magnetic entropy may be expressed as

$$S_m = Nk\left\{\log 2 - \frac{1}{2}(1+\sigma)\log(1+\sigma) - \frac{1}{2}(1-\sigma)\log(1-\sigma)\right\}. \qquad /2.19/$$

The lattice entropy is approximated as

$$S_l = R\alpha\varepsilon \quad , \qquad /2.20/$$

where

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad /2.21/$$

is the volume thermal expansion coefficient. Introducing the following dimensionless quantities

$$\Omega = \frac{A_l}{A_o} \quad , \qquad \omega = \frac{B_l}{A_o}$$

$$p = \frac{P}{A_o M_o^2} \quad , \qquad r = \frac{R}{A_o M_o^2} \quad , \qquad \tau = \frac{Nk\,T}{2A_o M_o^2} \qquad /2.22/$$

and

$$\theta = \frac{R\alpha}{Nk} \quad , \quad w(\sigma) = \frac{S_m}{Nk} \qquad /2.23/$$

the Gibbs free-energy can be written in the form

$$G = A_o M_o^2 \left\{ -\sigma^2 - \left[\Omega + \omega \left(\gamma + 2m^2 - 1 \right) \right] \sigma^2 \left(\varepsilon - \varepsilon_c \right) + \right.$$

$$\left. + \frac{1}{2} r\varepsilon^2 + p\varepsilon - 2\tau\theta\varepsilon - 2\tau W(\sigma) \right\} \quad , \qquad /2.24/$$

where A_o is a definitely positive quantity.

The equilibrium value of the deformation can be found from the equation

$$\frac{\partial G}{\partial \varepsilon} = 0 \quad . \qquad /2.25/$$

One gets

$$\varepsilon = 2 \frac{\theta}{r} \tau - \frac{p}{r} + \left(\Omega + \gamma\omega \right) \frac{\sigma^2}{r} + \frac{\omega}{r} \sigma^2 \left(2m^2 - 1 \right) \quad . \qquad /2.26/$$

The change of the deformation at the phase transition point is

$$\delta\varepsilon = \varepsilon(m=1) - \varepsilon(m=0) = \frac{2\sigma^2\omega}{r} \qquad /2.27/$$

the sign of which is determined by the sign of B_1. Making use of the expression /2.26/ for the Gibbs free-energy one can derive the formula

$$G = A_o M_o^2 \left\{ -\sigma^2 \left[1 + \frac{\mu}{r} \left(2\theta\tau - r\varepsilon_c - p \right) \right] - \frac{1}{2} \frac{\mu^2}{r} \sigma^4 - 2\tau w(\sigma) - \right.$$

$$\left. - \frac{1}{2} r \left(\frac{2\theta\tau - p}{r} \right)^2 \right\} , \qquad /2.28/$$

where

$$\mu = \Omega + \omega \left(\gamma + 2m^2 - 1 \right) . \qquad /2.29/$$

The relative sublattice magnetization per atom can be expressed from the equation

$$\frac{\partial G}{\partial \sigma} = 0 . \qquad /2.30/$$

After a short calculation one finds

$$\sigma = \text{th} \frac{h_{mol}}{\tau} , \qquad /2.31/$$

where

$$h_{mol} = \left[1 + \frac{\mu}{r} \left(2\theta\tau - r\varepsilon_c - p \right) \right] \sigma + \frac{\mu^2}{r} \sigma^3 . \qquad /2.32/$$

In the majority of the cases the ratio $\frac{\mu}{r}$ is smaller than one, and thus, making use of the inequality

$$q = \frac{\mu}{r} \left(\mu\sigma^2 + 2\theta\tau - r\varepsilon_c - p \right) << 1 \qquad /2.33/$$

one may expand G into a power series of q and it seems to be enough to retain the terms not higher than linear only. To do this, first of all, we rewrite /2.31/ in the form

$$\sigma = \sigma_o + \sigma_1 q \sim \sigma_o + \sigma_1 q_o \quad , \qquad /2.34/$$

where

$$q_o = \frac{\mu}{r} \left(\mu\sigma_o^2 + 2\theta\tau - r\varepsilon_c - p \right) \qquad /2.35/$$

and

$$\sigma_o = \text{th} \frac{\sigma_o}{\tau} \quad . \qquad /2.36/$$

The Gibbs free-energy is given by

$$G(\sigma,m) = G_o\,(\sigma_o,0) + q_o\, G_1\,(\sigma_o,m) + O(q_o^2) \; . \qquad /2.37/$$

A short calculation shows that the linear corrections to σ^2 and $2\tau\, w(\sigma)$ cancel out each other, and thus, we get

$$G_o(\sigma_o,0) = A_o M_o^2 \left\{ -\sigma_o^2 - 2\tau\, w(\sigma_o) - \frac{1}{2}\, r \left(\frac{2\theta\tau - p}{r} \right)^2 \right\} \qquad /2.38/$$

and

$$G_1(\sigma_o m) = -\frac{1}{2}\, A_o M_o^2 \sigma_o^2 \left(1 + \frac{2\theta\tau - r\varepsilon_c - p}{\mu\sigma_o^2 + 2\theta\tau - r\varepsilon_c - p} \right) . \qquad /2.39/$$

The second term in the right side of /2.37/ can be reexpressed in the form

$$q_o\, G_1(\sigma_o,m) = A_o M_o^2 \sigma_o^2 \omega\delta\varepsilon_o \; \{ f(m,u) + f_o(u) \} \; , \qquad /2.40/$$

where

$$f(m,u) = -m^4 + \left(1 - \frac{u}{\omega} \right) m^2 \qquad /2.41/$$

and

$$f_o(u) = \frac{1}{2}\left(1 - \gamma - \frac{\Omega}{\omega}\right)\left\{\frac{u}{\omega} - \frac{1}{2}\left(1 + \gamma + \frac{\Omega}{\omega}\right)\right\} \qquad /2.42/$$

Here, we introduced the notation

$$u = \frac{2\theta\tau - r\varepsilon_c - p}{\sigma_o^2} + \Omega + \gamma\omega. \qquad /2.43/$$

One may see from /2.40/ that the reduced free-energy $f(m,u)$ has to be used for the investigation of phase transitions characterized by different values of γ, listed in Table III. In very fortunate cases the relative magnetization σ_o doesn't vary significantly with the temperature in neighbourhood of the transition point, and thus, the parameter u introduced by /2.43/ may be regarded as a linear function of temperature. In the following this linear dependence will be assumed unless the refinement of the theory will not require a more realistic dependence.

3. PHASE TRANSITIONS WITH CONSTANT σ_o

Making use of the preceding model we should like to apply it for the phase transitions between antiferromagnetic structures. In this case the first task is to find the necessary and sufficient conditions for the loss and onset of the stability in the states $m = 0$ /or $m = 1$/, and $m = 1$ /or $m = 0$/, respectively.

The considerations are very trivial, nevertheless, a short review of them will be useful for the better understanding of physical content of the theory.

The equilibrium value of the parameter m has to be chosen from the roots of the equation

$$\frac{df}{d\theta} = 2m \left(1-m^2\right)^{1/2} \left(1 - \frac{u}{\omega} - 2m^2\right) = 0 \qquad /3.1/$$

which has three solutions, namely

$$m_1 = 0 \; ; \quad m_2 = \sqrt{\frac{1}{2}\left(1 - \frac{u}{\omega}\right)} \; ; \quad m_3 = 1 \; . \qquad /3.2/$$

The physically allowed θ values in these solutions have to satisfy the condition $0 \leq \theta \leq \frac{\pi}{2}$.

Let us follow the variation of the parameter m in the equilibrium state with increasing $\frac{u}{\omega}$. /As it was mentioned already $\frac{u}{\omega}$ is a linear function of temperature, if σ_o is constant within the temperature interval under consideration./ If $\frac{u}{\omega} < -1$, then among the solutions /3.2/ only two, namely m_1 and m_3 have physical meaning, $m = m_1$ minimizing the reduced free energy since

$$\frac{d^2f}{d\theta^2} = \begin{cases} 2\left(1 - \frac{u}{\omega}\right), & \text{if } m = m_1 \\ 2\left(1 + \frac{u}{\omega}\right), & \text{if } m = m_3 \; . \end{cases}$$

The second solution gives $m_2 > 1$, therefore it has to be excluded.

When $-1 \leq \frac{u}{\omega} \leq 1$, then among the solutions /3.2/ satisfying the condition $0 \leq \theta \leq \frac{\pi}{2}$, two, corresponding to $m = m_1$ and $m = m_3$, minimize, while the third $m = m_2$ maximizes the free energy as one can see from the expression

$$\frac{d^2 f}{d\theta^2} = \begin{cases} 2\left(1 - \frac{u}{\omega}\right), & \text{if} \quad m = m_1 \\ -2\left(1 - \frac{u^2}{\omega^2}\right), & \text{if} \quad m = m_2 \\ 2\left(1 + \frac{u}{\omega}\right), & \text{if} \quad m = m_3 \end{cases} .$$

The maximum between the two minima hinders the transitions. The free energy of the state $m = m_3$ is equal to that of the state $m = m_1$ at temperature $\frac{u}{\omega} = 0$, but the actual phase transition $m_1 \to m_3$ takes place only at that temperature where the energy barrier between the states disappears. Since

$$f(m,\tau) = \begin{cases} 0, & \text{if} \quad m = m_1 \\ \frac{1}{4}\left(1 - \frac{u}{\omega}\right)^2, & \text{if} \quad m = m_2 \\ -\frac{u}{\omega}, & \text{if} \quad m = m_3 \end{cases}$$

the $m_1 \to m_3$ transition will be realized when

$$u\,(1 \to 3) - \omega = 0 \quad . \qquad /4.3/$$

Finally, if $\frac{u}{\omega} > 1$, then again only two solutions, namely $m = m_1$ and $m = m_3$ have physical meaning and the free energy is minimized by $m = m_3$. The solution m_2 is imaginary and therefore it must be excluded.

Now, when we follow the change of the equilibrium value of the parameter m in the direction of decreasing temperature we find quite a similar picture. At the temperature $\frac{u}{\omega} = 0$ the free energy of the phase $m = m_1$ becomes the same as that of the phase $m = m_3$, transition, however, can't be observed because the energy maximum between the coexisting phase hinders the transition process. The phase transformation actually takes place at that temperature, where the system's free energy in the state $m = m_3$ will be equal to that in the maximum. This condition is nothing, but

$$-\frac{u}{\omega} = \frac{1}{4}\left(1 - \frac{u}{\omega}\right)^2 ,$$

i.e.

$$u\,(3 \to 1) + \omega = 0 \quad . \qquad /3.4/$$

If $\omega > 0$ /i.e. $B_1 > 0$/, then

$$u\,(1 \to 3) > u\,(3 \to 1) \quad .$$

The opposite inequality is valid when $\omega < 0$. In the next chapters we will use the following notations:

$$\begin{aligned} u_{sup} &= \max \{\, u\,(1 \to 3) \;\; ; \;\; u\,(3 \to 1)\} \\ u_{inf} &= \min \{\, u\,(1 \to 3) \;\; ; \;\; u\,(3 \to 1)\} \; . \end{aligned} \qquad /3.5/$$

The equilibrium temperature u_e where the two phases coexist, lies between the upper and lower transition temperatures. /In our case $u_e = 0$./

The ferromagnetic $\rightleftarrows$ antiferromagnetic transitions in absence of external magnetic field have to be treated in a similar way.

The dependence of the reduced Gibbs potential on the parameter m is shown in Fig.4 for different values of $\frac{u}{\omega}$.

The variation of the equilibrium value of m with temperature in the ideal case is illustrated in Fig.5 /see the full line/.

From the equations /3.3/ and /3.4/ one gets

$$T_{sup} = T_e(P) + \frac{1}{2}\frac{\delta\varepsilon_o}{\alpha} \quad ; \quad T_{inf} = T_e(P) - \frac{1}{2}\frac{\delta\varepsilon_o}{\alpha} \quad , \qquad /3.6/$$

where

$$T_e(P) = \frac{1}{2}\frac{P}{R\alpha} + \frac{1}{2}\frac{\varepsilon_c}{\alpha} - \frac{1}{2}\frac{\Omega + \gamma\omega}{R\alpha} A_o M_o^2 \sigma_o^2 \quad . \qquad /3.7/$$

Introducing the expression for the dilation discontinuity at the transition temperature the width of the temperature hysteresis can be given in the following form

$$T_{sup} - T_{inf} = \frac{\delta\varepsilon_o}{\alpha} \quad . \qquad /3.8/$$

This formula is valid only if the sublattice magnetization σ_o hardly changes in the interval $T_{inf} < T < T_{sup}$. The equivalent width in pressure is

$$P_{sup} - P_{inf} = 2R\delta\varepsilon_o \, . \qquad /3.8/$$

In practical cases the sharpness of the transition is rather smoothed because of more or less inhomogeneity in internal stresses existing in any real crystal. /See the dashed line in Fig. 4./ As a result of this inhomogeneity one may expect a definite cant in the hysteresis-loop. The canting angle ϕ is nothing, but

$$\phi = \text{arc ctg} \frac{\langle(\delta P)^2\rangle^{1/2}}{2R\alpha} \, , \qquad /3.9/$$

where $\langle(\delta P)\rangle^2$ is the mean squared deviation of the local pressure.

From the $u_e = 0$ one may see that the coexistence temperature, i.e. the temperature, where the Gibbs potentials of both phases $m = 0$ and $m = 1$ are equal, satisfies the equation

$$\frac{dT_e}{dP} = \frac{1}{2R\alpha} \qquad /3.10/$$

what is exactly the same as that derived from the Clausius-Clapeyron equation if one assumes that the discontinuous change in entropy is due to the discontinuous change in lattice parameter only. The latent heat is given by

$$Q_1 = T_e R\alpha\delta\varepsilon_o \ . \qquad /3.11/$$

In order to extend our investigations to the case of antiferromagnetic ⇄ ferromagnetic transitions in external magnetic field one has to add to the Gibbs free energy /2.34/ a new term expressing the interaction between the magnetic moments and field. Denoting by $\bar{M}_a$ and $\bar{M}_b$ the magnetization per atom in the sublattice a and b , one can write this additional term in the form

$$G_H = -\frac{1}{2} N \bar{H} \left(\bar{M}_a + \bar{M}_b\right) \ . \qquad /3.12/$$

Let us introduce the vectors

$$\bar{l} = \frac{\bar{M}_a - \bar{M}_b}{2M_o\sigma} \qquad \text{and} \qquad \bar{m} = \frac{\bar{M}_a + \bar{M}_b}{2M_o\sigma} \qquad /3.13/$$

where

$$M_o\sigma = |\bar{M}_a| = |\bar{M}_b| \ . \qquad /3.14/$$

If one neglects the magnetic anisotropy in the crystal then the vector $\bar{l}$ is perpendicular and the vector $\bar{m}$ is parallel to the external field direction, therefore instead of /3.12/ one gets

$$G_H = -2A_o M_o^2 \sigma \ hm \qquad /3.15/$$

where

$$h = \frac{1}{2} \frac{NH}{A_o M_o} \qquad /3.15/$$

and here m is the absolute value of $\bar{m}$. The role of m is the same as in /2.10/ but in this case it has a definite physical meaning, m being the net magnetization of the antiferromagnetic phase. One has to note that in the majority of the practically important cases the order of magnitude of h is the same as that of $\frac{\mu}{r}$. Therefore, instead of /3.15/ we write

$$G_H \sim -2A_o M_o^2 \sigma_o hm \quad . \qquad /3.16/$$

One may expect that the presence of the external magnetic field will promote the antiferromagnetic → ferromagnetic transition. Near the coexistence temperature a relatively weak magnetic field may already produce a significant net magnetization. In other words, it means that with the increasing magnetic field the antiferromagnetically coupled moments gradually turn into the field direction, i.e. the angle between the moments decreases. However, in contrary to the usual behaviour of the antiferromagnets, in this case the angle between the moments decreases to a definite, temperature dependent value only at which the umbrellalike antiferromagnetic structure will suddenly collapse, and thus, a simple ferromagnetic structure will be formed.

If the transition is induced by temperature variation in the presence of magnetic field the character of the variation in m will be the same as in the former case.

With help of /3.15/ the reduced free energy may be written in the form

$$f\,(m,u,\Delta) = -m^4 + \left(1 - \frac{u}{\omega}\right) m^2 - 2\,\frac{\Delta}{\omega^2}\,m \quad , \qquad /3.17/$$

where

$$\frac{\Delta}{\omega^2} = \frac{h}{\sigma_o \omega \delta \varepsilon_o} \quad . \qquad /3.18/$$

The reduced free energy versus "magnetization" at a given temperature but different magnetic fields is shown in Fig. 6, while in Fig. 7 similar curves can be seen but now the magnetic field is constant and the temperature is changing from curve to curve. The value of ω has been supposed to be positive and this means that the ferromagnetic state is stable at $u > 0$ in the absence of magnetic field. One may see in Fig. 6 that at a given field the free energy of the ferromagnetic state is equal to that of the antiferromagnetic state, nevertheless, the two states are energetically separated, i.e. the phase transition is hindered. Further increase in magnetic field is needed to overcome the energy barrier of elastic origin. The situation is quite similar in the case illustrated in Fig. 7 but the role of the magnetic field is replaced here by that of the temperature.

In the following we are going to calculate the field

dependence of the coexistence temperature and also that of the upper and lower transition temperatures. In order to do this we have to find first of all the conditions for the existence of physical solutions of the equation

$$\frac{df}{d\theta} = 2\left[-2m^3 + \left(1 - \frac{u}{\omega}\right) m - \frac{\Delta}{\omega^2}\right] \frac{dm}{d\theta} = 0 \ . \qquad /3.19/$$

It is clear that one has to deal with the solutions satisfying the inequality $0 \leq m \leq 1$. Denote by m_1, m_2, m_3 the roots of the third-order equation

$$-m^3 + \frac{1}{2}\left(1 - \frac{u}{\omega}\right) m - \frac{1}{2}\frac{\Delta}{\omega^2} = 0 \ , \qquad /3.20/$$

and let m_4 be the solution of the equation $\frac{dm}{d\theta} = 0$. Taking into account the condition

$$\frac{d^2f}{d\theta^2} = 2\left[-6m^2 + 1 - \frac{u}{\omega}\right]\left(\frac{dm}{d\theta}\right)^2 + 4\left[-m^3 + \frac{1}{2}\left(1 - \frac{u}{\omega}\right)m - \right.$$

$$\left. - \frac{1}{2}\frac{\Delta}{\omega^2}\right] \frac{d^2m}{d\theta^2} > 0 \qquad /3.21/$$

one may find immediately the minimizing solutions.

It is easy to show that among the roots m_1, m_2, and m_3 only one is real if u and Δ satisfy the inequality

$$\left(1 - \frac{u}{\omega}\right)\left(\frac{4\omega^2}{\Delta}\right)^{2/3} < 6 \ . \qquad /3.22/$$

One has to note, however, that in this case the real root is always negative.

It follows from this that only the solution $m_4 = 1$, which corresponds to the ferromagnetic state, has physical meaning. Indeed, the root $m_4 = 1$ minimizes the free energy if

$$\left(\frac{d^2f}{d\theta^2}\right)_{m=m_4} = 2\left(1 + \frac{u}{\omega} + \frac{\Delta}{\omega^2}\right) > 0 \quad . \qquad /3.23/$$

This condition is always satisfied when the inequality /3.22/ is true. The proof is very elementary. Replace $\frac{u}{\omega}$ in /3.23/ from /3.22/ by the quantity $1 - 6\left(\frac{\Delta}{4\omega^2}\right)^{2/3}$ which is always smaller then $\frac{u}{\omega}$ and write down the inequality

$$1 + \frac{u}{\omega} + \frac{\Delta}{\omega^2} > 2 - 6\left(\frac{\Delta}{4\omega^2}\right)^{2/3} + 4\,\frac{\Delta}{4\omega^2} \quad .$$

Since

$$4x^3 - 6x^2 + 2 \geq 0 \quad ; \quad x = \left(\frac{\Delta}{4\omega^2}\right)^{2/3}$$

for every $x \geq 0$ the statement is proven. One has to notice that the ferromagnetic state, in accordance with /3.23/, remains stable for values u and Δ not satisfying the inequality /3.22/.

When instead of /3.22/ the inequality

$$\left(1 - \frac{u}{\omega}\right)\left(\frac{4\omega^2}{\Delta}\right)^{2/3} > 6 \qquad /3.24/$$

is true then all the three roots of /3.20/ are real and it is easy to show that

$$m_1 < -\sqrt{\frac{1}{6}\left(1 - \frac{u}{\omega}\right)} \qquad /3.25/$$

and

$$0 \leq m_2 \leq \sqrt{\frac{1}{6}\left(1 - \frac{u}{\omega}\right)} < m_3 \quad . \qquad /3.26/$$

Making use of these inequalities one can prove on the basis of /3.21/ that the free energy is minimized by the solution $m = m_2 = \tilde{m}$ and maximized by $m = m_3$. The solution $m = m_1$ has to be excluded because of its non-physical nature.

The umbrellalike solution $\tilde{m}$, which will be named simply as antiferromagnetic solution remains stable until

$$\tilde{m}^2 (u,\Delta) < \frac{1}{6}\left(1 - \frac{u}{\omega}\right) .$$

Instability sets in when

$$\tilde{m}^2 (u,\Delta) = \frac{1}{6}\left(1 - \frac{u}{\omega}\right) \qquad /3.27/$$

and then the antiferromagnetic phase suddenly transforms into the ferromagnetic one.

Elimintinating the net magnetization m in /3.20/ with help of /3.27/ one gets a very important equation for the field dependence of the antiferromagnetic → ferromagnetic transition temperature. This equation can be written in the form

$$\frac{\Delta}{4\omega^2} = \left[\frac{1}{6} \left(1 - \frac{u}{\omega} \right) \right]^{3/2} \quad . \qquad /3.28/$$

It follows from this that the local stability of the antiferromagnetic state in the presence of magnetic field breaks down when the temperature reaches a certain critical value

$$u_{sup} = \omega \left[1 - 6 \left(\frac{\Delta}{4\omega^2} \right)^{2/3} \right] . \qquad /3.29/$$

The onset of the stable ferromagnetic phase results in a discontinuous change of the net magnetization. Its maximal value in the antiferromagnetic state before the sudden change is

$$\tilde{m}_{sup} (\Delta) = \left(\frac{\Delta}{4\omega^2} \right)^{1/3} \quad . \qquad /3.30/$$

When the temperature is fixed and the increasing magnetic field brings about the transition one observes its start only at a certain critical value of the magnetic field, namely at

$$\Delta_{sup} = \frac{1}{3} \sqrt{\frac{2}{3}} \omega^2 \left(1 - \frac{u}{\omega} \right)^{3/2} \quad . \qquad /3.31/$$

In this case the maximal net magnetization in the antiferromagnetic state can be expressed by

$$\tilde{m}_{sup} (u) = \sqrt{\frac{1}{6} \left(1 - \frac{u}{\omega} \right)} \quad . \qquad /3.32/$$

Varying the temperature and magnetic field in opposite direction the ferromagnetic → antiferromagnetic transition will be observed when

$$1 + \frac{u}{\omega} + \frac{\Delta}{\omega^2} = 0$$

i.e. in a constant field the antiferromagnetism is going to appear at temperature

$$u_{inf} = -\omega \left(1 + \frac{\Delta}{\omega^2} \right) , \qquad /3.33/$$

where the net magnetization changes discontinuously from the value of $m = 1$ to that of

$$\tilde{m}_{inf} (\Delta) = \frac{1}{2} \left[\sqrt{1 + 2 \frac{\Delta}{\omega^2}} - 1 \right] . \qquad /3.34/$$

At constant temperature the stability of the ferromagnetic phase disappears when the magnetic field is lowered to

$$\Delta_{inf} = -\omega^2 \left(1 - \frac{u}{\omega} \right) . \qquad /3.35/$$

The parameter m shows a definite jump from $m = 1$ to

$$\tilde{m}_{inf} (u) = \frac{1}{2} \left[\sqrt{-\left(1 + 2 \frac{u}{\omega} \right)} - 1 \right] . \qquad /3.36/$$

Since both parameters Δ_{inf} and $\tilde{m}_{inf}$ must be positive one may produce a ferromagnetic → antiferromagnetic transition with decreasing magnetic field only if $\frac{u}{\omega} < -1$. In

other word, the magnetic field induced antiferromagnetic → ferromagnetic phase transition is reversible only when $\frac{u}{\omega} < -1$. In this case, lowering the magnetic field below the critical value Δ_{inf} the energy barrier separating the thermodynamically stable antiferromagnetic state from the ferromagnetic one disappears, making the way for the transition free.

In Fig. 8 one may see the coexistence curve $u_e(\Delta)$ between the curves $u_{sup}(\Delta)$ and $u_{inf}(\Delta)$. Along the curve $u_e(\Delta)$ the Gibbs free energy of the ferromagnetic phase is equal to that of the antiferromagnetic phase. Explicit formula for the coexistence curve can't be given; a parametric equation, however, can be easily derived. One finds

$$\frac{u_e}{\omega} = -\tilde{m}\,(2 + 3\tilde{m})$$

$$\frac{\Delta}{\omega^2} = \tilde{m}\,(1 + \tilde{m})^2 \quad , \qquad /3.37/$$

where $\tilde{m}$ is the solution of /3.20/. The coexistence curve $u_e(\Delta)$ reaches the curves $u_{sup}(\Delta)$ and $u_{inf}(\Delta)$ in the point

$$\frac{\Delta_t}{\omega^2} = 4 \quad , \quad \frac{u_t}{\omega} = -5 \quad , \qquad /3.38/$$

when u_t is higher than the absolute zero.
The first-order character of the phase transition disappears in this point. It is seen that when the magnetic

field is high enough, i.e.

$$4 \leq \frac{\Delta}{\omega^2} \leq \frac{\Delta_c}{\omega^2}$$

then the ferromagnetic $\rightleftarrows$ antiferromagnetic transition will be of second-order. One may expect large fluctuations of the parameter m when the transition is of second-order. In the point given by /3.38/ the quantity

$$\frac{d\tilde{m}}{d\Delta} = \frac{1}{\omega^2\left(1 - \frac{u}{\omega} - 6\tilde{m}^2\right)} \qquad /3.39/$$

which is proportional to the susceptibility, becomes infinite. One has to note that at fields higher than $\frac{\Delta_c}{\omega^2}$ the temperature variation does not result in a real phase transition, the only change is that the ferromagnetic phase transforms at $u = 0$ to a phase which is nothing but the antiferromagnetic phase in a magnetic field strong enough to turn the moments parallel to the field direction.

In the upper part of Fig. 8 the variation of the net magnetization of the antiferromagnetic phase along the coexistence curve is also shown. At the fields higher than $\frac{\Delta_t}{\omega^2}$ the net magnetization is equal to 1.

The phase transition is always of first-order and hindered if the parameters Δ and u satisfy the inequalities: $0 \leq \frac{\Delta}{\omega^2} < 4$ and $-5 < \frac{u}{\omega} \leq 1$, respectively.

The hindrance of the transition - as it was already pointed out - results in a definite hysteresis. The width of the thermal hysteresis depends on the magnetic field and as it can be seen from the expression

$$u_{sup} - u_{inf} = 2\omega \left[1 + \frac{\Delta}{2\omega^2} - 3 \left(\frac{\Delta}{4\omega^2} \right)^{2/3} \right] \qquad /3.40/$$

it decreases with increasing field and vanishes at the field corresponding to the triple point. The same will be true for the temperature dependence of the magnetic hysteresis width, since

$$\Delta_{sup} - \Delta_{inf} = \omega^2 \left[1 + \frac{u}{\omega} + \frac{1}{3} \sqrt{\frac{2}{3}} \left(1 - \frac{u}{\omega} \right)^{3/2} \right] . \qquad /3.41/$$

In Fig. 8 the arrows intersecting the phase boundary illustrate the different types of phase transitions. The black points on the arrows indicate the parameters u and Δ characterizing the transition.

For sake of completeness we show in Fig. 9 the temperature dependence of the net magnetization in the

antiferromagnetic phase at various magnetic fields. One may see on the curves that the net magnetization suffers a sudden change from $\tilde{m}_{sup} \leq 1$ to $\tilde{m} = 1$ when the temperature u reaches a critical value u_{sup} due to a given magnetic field. The dashed curve in Fig. 9 shows the function $\tilde{m}_{sup}(u)$ which gives the maximal net magnetization available in antiferromagnetic state at constant temperature in an external magnetic field.

In Fig. 10 the magnetic field dependence of $\tilde{m}$ is illustrated at different temperatures. In contrary to the previous case, the dashed curve in this figure shows the maximum of the magnetization $\tilde{m}_{sup}(\Delta)$ available in the antiferromagnetic phase with increasing temperature but at constant magnetic field.

Finally, it seems to be useful to rewrite the most important formulas in such a way that only directly measurable quantities should occur in them. Making use of the expressions /2.27/ and /3.6/ one gets from /3.29/ and /3.33/ the formulas:

$$T_{sup}(H) = T_{sup} - 3\left(T_{sup} - T_{inf}\right)\left(\frac{H}{H_t}\right)^{2/3} \qquad /3.42/$$

and

$$T_{inf}(H) = T_{inf} - 2\left(T_{sup} - T_{inf}\right)\frac{H}{H_t} \qquad /3.43/$$

where

$$H_t = 4 \left(T_{sup} - T_{inf}\right)^2 \frac{R\alpha^2}{NM_o\sigma_o} \qquad /3.44/$$

is the magnetic field due to the triple point. The triple point temperature T_t can be expressed in a very simple form, namely

$$T_{sup}\,(H_t) = T_{inf}\,(H_t) = T_t = 3T_{inf} - 2T_{sup} \ . \qquad /3.45/$$

The temperatures T_{sup} and T_{inf} may be obtained from measurements without magnetic field.

4. VARIATION OF THE AVERAGE MAGNETIZATION PER ATOM

Let us examine, first of all, the correction term to the magnetization per atom. To get self-consistent solution we write the equation /2.31/ in the form

$$\sigma = \sigma_o + \sigma_1 q = \text{th}\,\frac{\sigma_o + (\sigma_o+\sigma_1)\,q}{\tau} \sim \sigma_o + \left(1-\sigma_o^2\right)\left(\sigma_o+\sigma_1\right)\frac{q}{\tau} \qquad /4.1/$$

and replacing q by q_o we get

$$\delta\sigma = \sigma_1 q_o = \frac{\mu}{r}\,\sigma_o\,\frac{\lambda}{1-\lambda}\left(\mu\sigma_o^2 + 2\theta\tau - r\varepsilon_c - p\right) , \qquad /4.2/$$

where

$$\lambda = \frac{1-\sigma_o^2}{\tau} \ . \qquad /4.3/$$

It can be easily shown that λ is a monotonously increasing function of τ in the interval $0 \leq \tau \leq 1$. One finds that

$$\lim_{\tau \to 0} \lambda(\tau) = 0 \qquad \text{and} \qquad \lim_{\tau \to 1} \lambda(\tau) = 1 \quad . \qquad /4.4/$$

From /4.2/ one may see that the value of magnetization per atom at the coexistence temperature, i.e. where

$$2\theta\tau_e - r\varepsilon_c - p = -(\Omega + \gamma\omega)\,\sigma_o^2 \qquad /4.5/$$

is not the same in the phases $m = 1$ and $m = 0$. We find

$$\delta\sigma_e(m = 1) = \frac{\omega[\Omega + (1+\gamma)\,\omega]}{r} \frac{\lambda_e}{1-\lambda_e} \sigma_{oe}^3 \qquad /4.6/$$

and

$$\delta\sigma_e(m = o) = -\frac{\omega[\Omega - (1-\gamma)\,\omega]}{r} \frac{\lambda_e}{1-\lambda_e} \sigma_{oe}^3 \quad , \qquad /4.7/$$

where the subscript e indicates that each temperature dependent quantity should be taken at the coexistence temperature. The discontinuous change in magnetization per atom brings about a similar change in magnetic entropy too, which leads obviously to the appearance of a magnetic latent heat contribution. This is given by

$$Q_m = -4A_o M_o^2 \frac{\omega(\Omega + \gamma)}{r} \frac{\lambda_e}{1-\lambda_e} \sigma_{oe}^4 \; T_e \quad . \qquad /4.8/$$

As it was mentioned already, the phase transition is hindered, and thus, the formation of the phase $m = 1$ takes place only at the temperature $\tau = \tau_{sup}$. The change in the magnetization per atom at this temperature can be expressed by

$$\sigma(m=1,\ \tau=\tau_{sup}) - \sigma(m=o,\ \tau=\tau_{sup}) = [\Omega+(1+\gamma)\omega]\ \frac{\lambda_s}{1-\lambda_s}\ \sigma_{os}\ \delta\varepsilon_{os}\ , \qquad /4.9/$$

where the subscript s indicates that each temperature dependent quantity should be taken at the temperature $\tau = \tau_{sup}$. A similar discontinuous change in the magnetization has to be expected at the temperature $\tau = \tau_{inf}$ where the inverse transition takes place. One gets

$$\sigma(m=1,\ \tau=\tau_{inf}) - \sigma(m=o,\ \tau=\tau_{inf}) = [\Omega-(1-\gamma)\omega]\ \frac{\lambda_i}{1-\lambda_i}\ \sigma_{oi}\ \delta\varepsilon_{oi}\ , \qquad /4.10/$$

where the subscript i shows again that each temperature dependent quantity is taken at $\tau = \tau_{inf}$. The schematic behaviour of the temperature dependence of σ is shown in Fig. 11 when $\Omega = \gamma = 0$.

In chapter 3 we derived a simple formula for the discontinuous change of the lattice distortion /see /2.27//. Now, taking into account the magnetization change we would like to refine this formula. A short calculation shows that at the transition temperature $\tau = \tau_{sup}$ we should write

$$\delta\varepsilon_s = \delta\varepsilon_{cs}\left\{1+\left(2+\gamma+\frac{\Omega}{\omega}\right)\left[\Omega+(1+\gamma)\omega\right]\frac{\lambda_s}{1-\lambda_s}\sigma_{os}\,\delta\varepsilon_{os}\right\} \quad /4.11/$$

and similarly at $\tau = \tau_{inf}$ we get

$$\delta\varepsilon_i = \delta\varepsilon_{oi}\left\{1-\left(2-\gamma-\frac{\Omega}{\omega}\right)\left[\Omega-(1-\gamma)\omega\right]\frac{\lambda_i}{1-\lambda_i}\sigma_{oi}\,\delta\varepsilon_{oi}\right\}. \quad /4.12/$$

The corrections both in /4.11/ and /4.12/ are usually small, nevertheless, it seems useful to take into account these corrections in evaluating the parameters Ω and ω from the measured data of $\delta\varepsilon$.

Making use of the results obtained for the discontinuous change of σ the equation /4.5/ giving the coexistence temperature can be also refined. It is not necessary to reproduce here the details of calculations since they are very elementary, it is better to cite the final result. The corrected equation can be written in the form

$$\tau_e = \frac{r\varepsilon_c}{2\theta} + \frac{p}{2\theta} - \frac{\Omega+\gamma\omega}{2\theta}\sigma_{oe}^2\left\{1+(\Omega+\omega)\frac{\lambda_e}{1-\lambda_e}\delta\varepsilon_{oe}\right\}. \quad /4.13/$$

One may see from this that in the case of non-vanishing Ω and γ the pressure coefficient of τ_e is given by

$$\frac{d\tau_e}{dp} = \frac{1}{2\theta}\,\frac{1}{1+\frac{\Omega+\gamma\omega}{\theta}\sigma_{oe}\frac{d\sigma_{oe}}{d\tau_e}} \quad /4.14/$$

if one neglects the small correction term in /4.13/. The second factor in the right side of this formula may become

very large when $\Omega + \gamma\omega > 0$ since $\frac{d\sigma_{oe}}{d\tau_e} < 0$. Therefore, in most cases the expression for $\frac{d\tau_e}{dp}$ given earlier by /3.10/ must be replaced by /4.14/.

Now, we have to discuss in more details the influence of the temperature dependence of σ_o on the transition. In the preceding considerations we dealt only with the discontinuous change in σ but doing this we always assumed the variation of σ_o in the interval $\tau_{inf} \leq \tau \leq \tau_{sup}$ to be small. In addition to this we supposed the inequality

$$\frac{\delta\sigma}{\sigma_o} << 1$$

to be satisfied also in the whole temperature range $0 \leq \tau \leq \tau_{sup}$. The correction $\delta\sigma$ derived by linear approximation in q is obviously wrong near the ordering temperature, since σ_o tends to zero, and unfortunately, $\delta\sigma$ goes to infinity. One has to note, that this behaviour of $\delta\sigma$ is a direct consequence of the limited validity of the linear approximation. Nevertheless, if we would like to use in our consideration corrections linear in q only, we have to indicate the temperature limit below which the linear approximation is certainly correct. This problem can be solved easily in a slightly reformulized manner by requiring the linear approximation to be valid until $\tau > \tau_{sup}$ and thence deriving a criterion for the basic parameter of the theory. Proceeding from /4.9/ we get

$$\sigma_{os}^2 \frac{\lambda_s}{1-\lambda_s} << \frac{1}{2} \frac{r}{\omega[\Omega + (1+\gamma)\omega]} \quad . \qquad /4.15/$$

Using this inequality one can always decide for a given set of parameters whether the linear approximation is true or not below the temperature τ_{sup}.

In order to say more about the temperature dependence of $\delta\sigma$ one should rewrite the expression /4.2/ in the form

$$\delta\sigma(\sigma_o) = \sigma_o \left(1-\sigma_o^2\right) \frac{2a\sigma_o + \left(b\sigma_o^2 - a\tau_e\right) \log \frac{1+\sigma_o}{1-\sigma_o}}{2\sigma_o - \left(1-\sigma_o^2\right) \log \frac{1+\sigma_o}{1-\sigma_o}} \quad , \qquad /4.16/$$

where

$$a = \frac{2\mu\theta}{r} \qquad \text{and} \qquad b = \frac{\mu}{r}\,\omega\left(2m^2 - 1\right) \quad . \qquad /4.17/$$

One may see immediately that

$$\lim_{\sigma_o \to o} \sigma_o\, \delta\sigma\,(\sigma_o) = a\,(1 - \tau_e) \qquad /4.18/$$

i.e.

$$\lim_{\sigma_o \to o} \delta\sigma(\sigma_o) = \begin{cases} +\infty\,, & \text{if} \quad \mu > 0 \\ -\infty\,, & \text{if} \quad \mu < 0\,. \end{cases} \qquad /4.19/$$

An other interesting property follows from /4.16/ when σ_o is approaching its saturation value. The correction term $\delta\sigma$ becomes zero at $\sigma_o = 1$ but its first derivative with σ_o

$$2\theta - r\varepsilon_c - p > 0 \quad . \qquad /4.25/$$

In order to ensure the second-order character of the disappearance of σ one has to require the fulfilment of the condition

$$\frac{d^2G}{d\sigma^2} \geq 0 \quad , \qquad /4.26/$$

which can be rewritten in the form

$$\tau_c \geq 3\,\frac{\mu^2}{r} \quad . \qquad /4.27/$$

One has to mention that in many cases the lattice distortion caused by the magneto-elastic interaction is large enough to lead to a first-order transition in σ . In these cases, naturally, an inequality opposite to /4.27/ should be satisfied. In the Bean's paper /2/ a simplest version of this was already discussed.

In the following we will still suppose the disappearance of σ to be of second-order, and try to find the conditions for the existence of a triple point in the T-P place. To do this we should derive, first of all, the pressure dependence of the coexistence temperature. From

$$G\,(m=1) \;\; = G\,(m=o)$$

we get

$$\left(\tau_e - 3\,\frac{\mu_1^2}{r}\right)\sigma_e^2\,(m=1) = \left(\tau_e - 3\,\frac{\mu_o^2}{r}\right)\sigma_e^2\,(m=o) \qquad /4.28/$$

which - making use of the expression /4.23/ - gives the unknown pressure dependence $\tau_e(p)$. In order to find the "coordinates" of the triple point in the T-P plane it is not necessary to solve the equation /4.28/ because it can be immediately seen that

$$\tau_c\,(m=1) = \tau_c\,(m=o) = \tau_e = 1 \qquad /4.29/$$

when the equation

$$2\theta - r\varepsilon_c - p = 0 \qquad /4.30/$$

is satisfied. In other words, the curves $\tau_c\,(m=1,\ p)$, $\tau_c\,(m=o,\ p)$ and $\tau_e(p)$ have a common point /this is the triple point/ at the pressure

$$p_t = 2\theta - r\varepsilon_c \quad . \qquad /4.31/$$

In Fig. 13 the typical phase boundaries and the position of the triple point are shown. There is an interesting possibility for changing the order of phase transition at the triple point. Let us suppose the transition from the state $m = 1$ to the paramagnetic one to be of second-order even very near the triple point. This means that the inequality

$$3\,\frac{\mu_1^2}{r} < 1 \qquad /4.32/$$

has to be satisfied. Further, let us assume that the transition from the state $m = 0$ to the paramagnetic one is of first-order, i.e.

$$3\,\frac{\mu_o^2}{r} > 1 \qquad /4.33/$$

when $\gamma = 0$ and the sign of Ω is different from that of ω both inequalities can be satisfied if

$$\Omega^2 + \omega^2 = \frac{1}{3}\,r \quad . \qquad /4.34/$$

In order to ensure the fulfilment of /4.34/ both Ω and ω must be fairly large, nevertheless, μ_1 remains small enough because it is nothing, but the difference of Ω and ω. The possible change in order of the disappearance of σ is of great importance in understanding some of the recent observations [11].

5. FINAL REMARKS

The previous very elementary consideration can be sucessfully applied in many cases listed in Table I. Nevertheless, one should keep in mind that nobody can expect quantitative but only qualitative agreement between the theoretical and experimental results and therefore we don't want make here any detailed comparison between the theory and experiments, however, it seems to be worth while to mention one example which has been in the centre of interest since the last five - six years.

This example is the iron-rhodium alloy of equiatomic composition which is ferromagnetic at high and antiferromagnetic at low temperatures. The alloy possesses a body-

centred cubic lattice in which the chemical order is of CsCl type and the magnetic structure in the antiferromagnetic state coincides with the structure Af I shown in Fig. 3. This is the so-called G-Type structure in which every positive Fe spin is surrounded by six negative Fe spins. The magnetic unit cell edge is thus double that of the chemical cell. The Rh atom, which is located at the body-centered position is now surrounded by four positive and four negative Fe spins. Thus the Rh moment may not be ordered. Indeed, according to the neutron diffraction measurements [12] the existence of a non-zero magnetic moment at the Rh sites in the antiferromagnetic state can be excluded.

It is of interest to note that it can be shown on pure theoretical basis that the average magnetic moment of the Rh atoms must be zero if the iron lattice possesses a collinear antiferromagnetic structure. To do this it is enough to assume the existence of a triple point in the T-P phase diagram similar to that in Fig. 13 and the second-order character of the antiferromagnetic → paramagnetic phase transition occuring at pressures higher than the triple point pressure. On the basis of these assumptions making use of the group-theoretical methods one can prove the disappearance of the Rh moment. The proof was done by Hargitai [13] several years ago and the existence of the triple point in the T-P plane was experimentally shown by Wayne [11] very recently. One has to mention, however, that the meas-

urements of Wayne unfortunately indicate the antiferromagnetic → paramagnetic phase transition to be of first-order the possibility of that we discussed in chapter 4. This fact alters the situation because the Landau theory can't be applied in this case, however, the existence of a zero effective exchange field at the Rh sites further suggests the Rh moments must be zero. In the ferromagnetic state the Rh atoms have a fairly large magnetic moment /$\mu_{Rh} \sim 1{,}0\ \mu_B$/ which has to play an important role in the phase transition.

The antiferromagnetic ⇄ ferromagnetic phase transition is of first-order and is associated with a relatively large discontinuous change of the lattice parameter. In Fig. 14 the temperature dependence of the lattice parameter measured by Zsoldos [14] is shown. The specimen with 49,6 at. per cent rhodium was prepared by melting and quenched in water after 10 hours annealing at 1000°C. One may see the hysteresis width to be very small. In order to illustrate the influence of the inhomogeneities on the shape of the hysteresis loop the lattice parameter change in a chemically prepared powdered sample of equiatomic composition was also measured. The results of the measurements are shown in Fig. 15. One can observe the alteration of the hysteresis loop to be similar to that predicted in chapter 3 /see Fig. 4./.

In accordance with the theory both transition temperatures $T\,(AF \rightarrow F, P) = T_{sup}(P)$ and $T\,(F \rightarrow AF, P) = T_{inf}(P)$ increase with increasing pressure and the tem-

perature width of the hysteresis /i.e. the difference $T_{sup} - T_{inf}$/ decreases with increasing pressure if the transition in the triple point is of second-order.

Making use of the results of chapter 4 the properties of the magnetic field induced AF $\rightleftarrows$ F transition can be explained also very easily. One finds both transition temperatures $T_{sup}\,H$ and $T_{inf}\,H$ as well as the hysteresis width /i.e. $T_{sup} - T_{inf}$/ to decrease with increasing magnetic field. The values of the magnetic field and temperature, where the hysteresis disappears can be calculated from the experimental data.

It can be shown also that the transition AF $\rightarrow$ F induced by external magnetic field is not reversible above a given temperature. Indeed, we observed that after switching off the external magnetic field the thermodynamically unstable F state does not transform into the stable AF one because of the energy barrier between the minima corresponding to the AF and F phases.

In chapter 4 it was shown that the average magnetic moment per atom suffers a discontinuous change at both transition temperatures T_{sup} and T_{inf}. To observe this change by measuring the temperature dependence of the sublattice magnetization with the neutron diffraction technique seems to by very difficult because of the limited sensitivity of this technique. It is well-known, however, that

a small change in the atomic magnetic moment may produce a fairly large change in the internal field acting on the nucleus. In the iron-rhodium alloys the temperature dependence of the internal field at the iron nuclei was measured by several authors [15] and they found a definit jump in it at the transition temperature in good agreement with the theory.

In the preceding chapters we always neglected the influence of the magnetic behaviour of the rhodium atoms on the phase transition. It would be, however, a serious mistake to think that the onset of the rhodium moment in the ferromagnetic phase doesn't bring about any substantial influence on the thermodynamics of the phase transition. Now, we don't want to go here into the details of the problem, we would like to make only a few remarks.

It is obvious that the Rh atoms may have magnetic moment if the antiferromagnetic structure is not collinear. For instance, the presence of an external magnetic field induces a deviation of the moments from their antiparallel orientation and this results in a magnetic moment on the Rh atoms. The onset of the moment on Rh atoms will accelerate the AF → F transition. Indeed, the calculations show the transition temperature to be lower than in the former case if one takes into account of the magnetic properties of the Rh atoms.

Finally, one should not forget that in a collinear antiferromagnet, where the average exchange field is zero at the rhodium sites, the actual value of this field is never exactly zero but fluctuates about zero. This fluctuating exchange field produces a fluctuating moment on the rhodium atoms, and in turn, this will result in a fluctuating deviation of the iron moments from their antiparallel orientation. If the enhancement of the fluctuations is large enough the stability of the antiferromagnetic state may disappear, i.e. phase transition will take place.

In the stable antiferrogmagnetic state small fluctuations still exist and if the characteristic decay time of these fluctuations has the same order of magnitude as the period of the Larmor's precession of the iron nuclear moments, a line broadening in the Mössbauer spectrum has to be observed. This line broadening was found by Cser and Keszthelyi [16] in their very recent measurements. The physical situation is very similar to the Brownian-like motion, the fluctuating rhodium moment as a stochastic driving force induces random deviations of the iron moments from their antiparallel orientation. The details of these calculations will be published elswhere.

Figure Captions

1/ "Family tree" of magnetic phase transitions

2/ Lattice points with sublattice numbers

3/ Different structures and phase boundaries

4/ Dependence of the reduced Gibbs potential on the parameter of bending for different values of $\frac{u}{\omega}$

5/ Variation of the equilibrium value of m with temperature /the full line corresponds to the completely homogeneous transition while the dashed line to the inhomogeneous one/

6/ Reduced Gibbs free-energy versus "magnetization" at constant temperature but different magnetic fields

7/ Reduced Gibbs free-energy versus "magnetization" at constant magnetic field but different temperatures

8/ T-H /i.e. $\frac{u}{\omega} - \frac{\Delta}{\omega^2}$ / phase diagram and variation of the magnetization along the coexistence curve

9/ Net magnetization versus temperature at different magnetic field in antiferromagnetic state

10/ Net magnetization versus magnetic field at various temperatures in antiferromagnetic state

11/ Temperature dependence and discontinuous change of the average magnetic moment per atom

12/ Correction to average magnetic moment per atom versus σ_o

13/ T-P /i.e. τ-p/ phase diagram

14/ Lattice parameter versus temperature for FeRh with 49,6 at per cent Rh

15/ Lattice parameter versus temperature and hysteresis for chemically prepared FeRh of equiatomic composition

Table Captions

Table I	Some magnetic systems that exhibit transition of first-order
Table II	Eigen-values and eigen-vectors for different structures
Table III	Parameters for various transitions
Table IV	Characteristics of the temperature dependence of $\delta\sigma$

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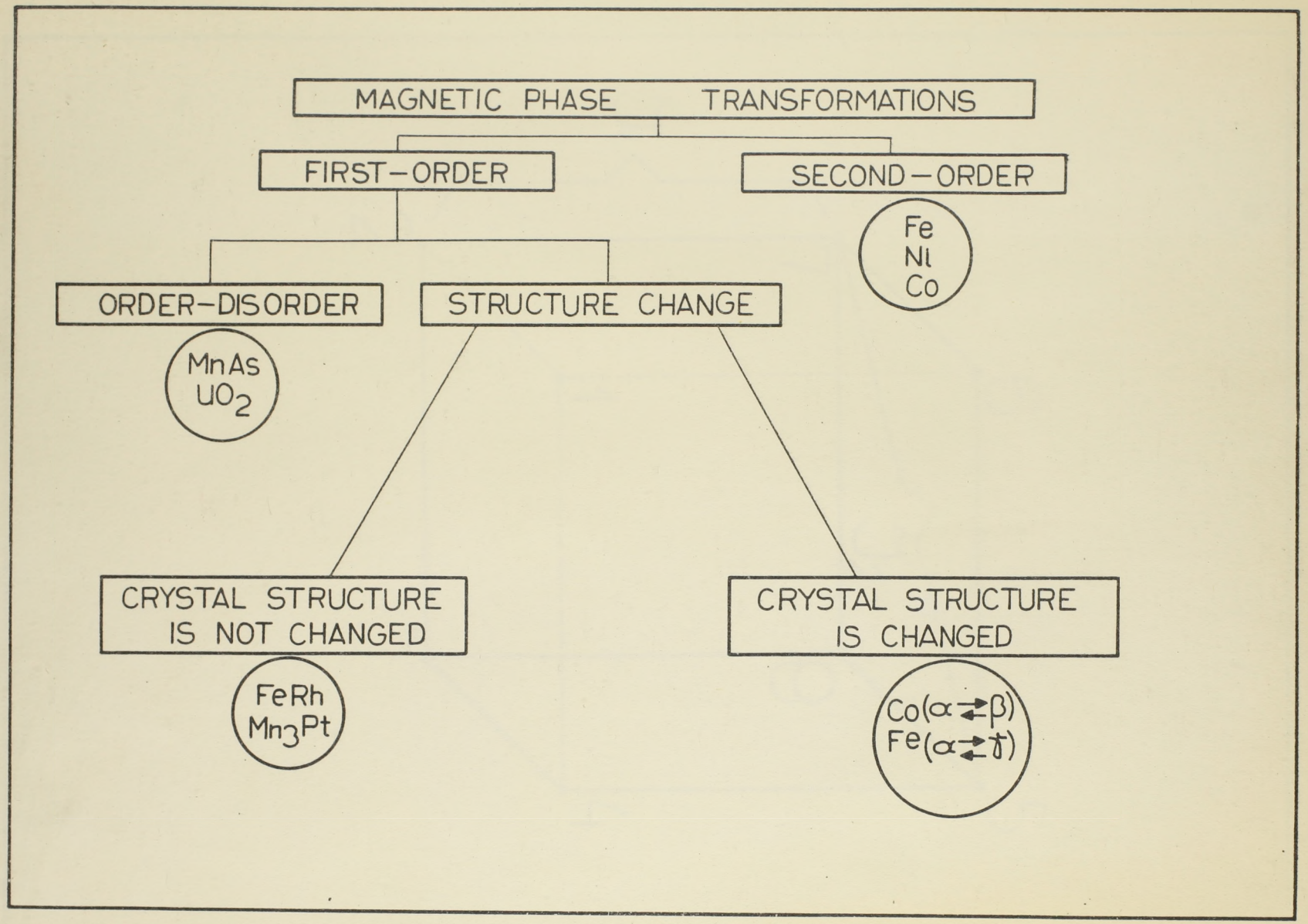

MAGNETIC PHASE TRANSFORMATIONS
FIRST–ORDER
SECOND–ORDER
Fe
Ni
Co
ORDER–DISORDER
STRUCTURE CHANGE
MnAs
UO_2
CRYSTAL STRUCTURE IS NOT CHANGED
CRYSTAL STRUCTURE IS CHANGED
FeRh
Mn_3Pt
$Co(\alpha \rightleftarrows \beta)$
$Fe(\alpha \rightleftarrows \gamma)$

Fig. 1

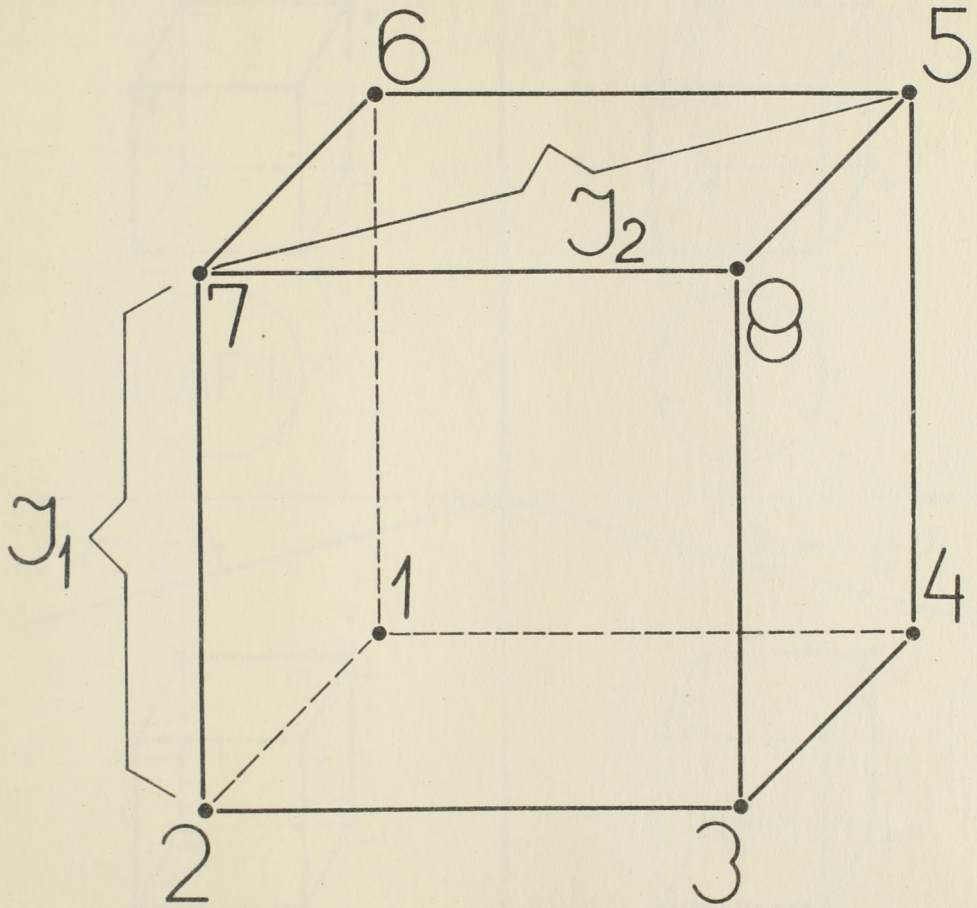


Fig. 2

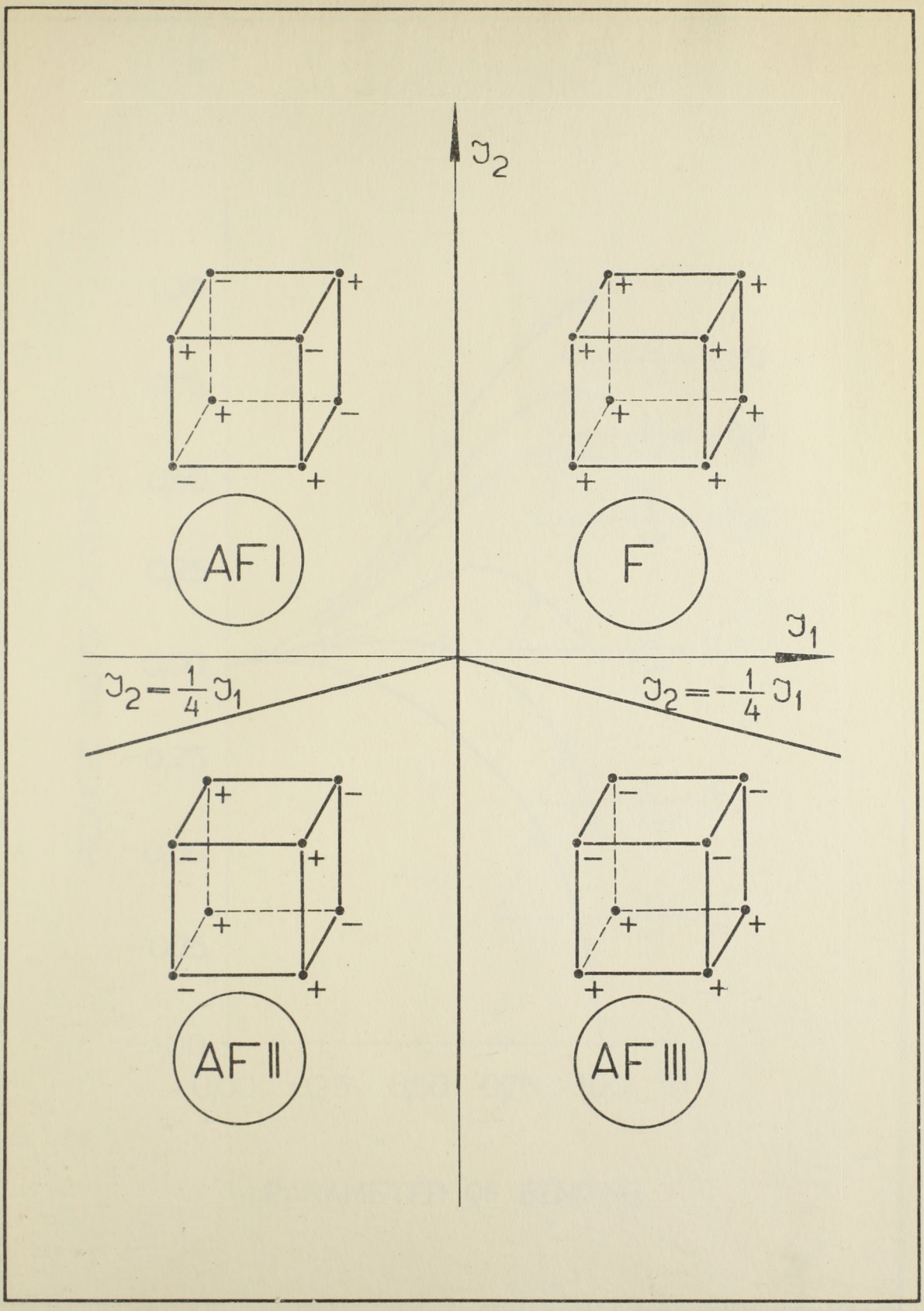

$\mathfrak{I}_2$
$\mathfrak{I}_1$
$\mathfrak{I}_2 = -\frac{1}{4}\mathfrak{I}_1$
$\mathfrak{I}_2 = \frac{1}{4}\mathfrak{I}_1$
AF I
F
AF II
AF III

Fig. 3

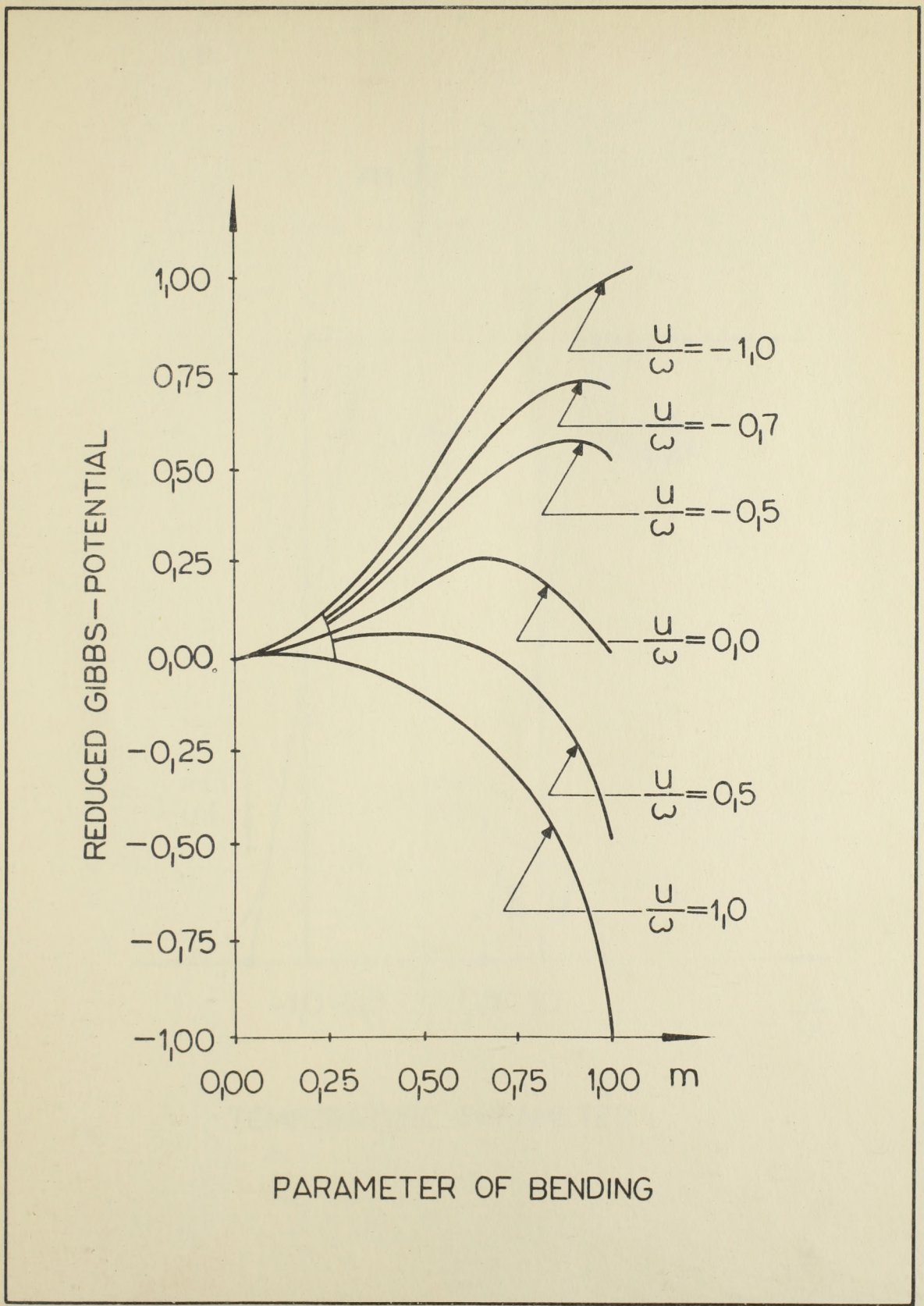
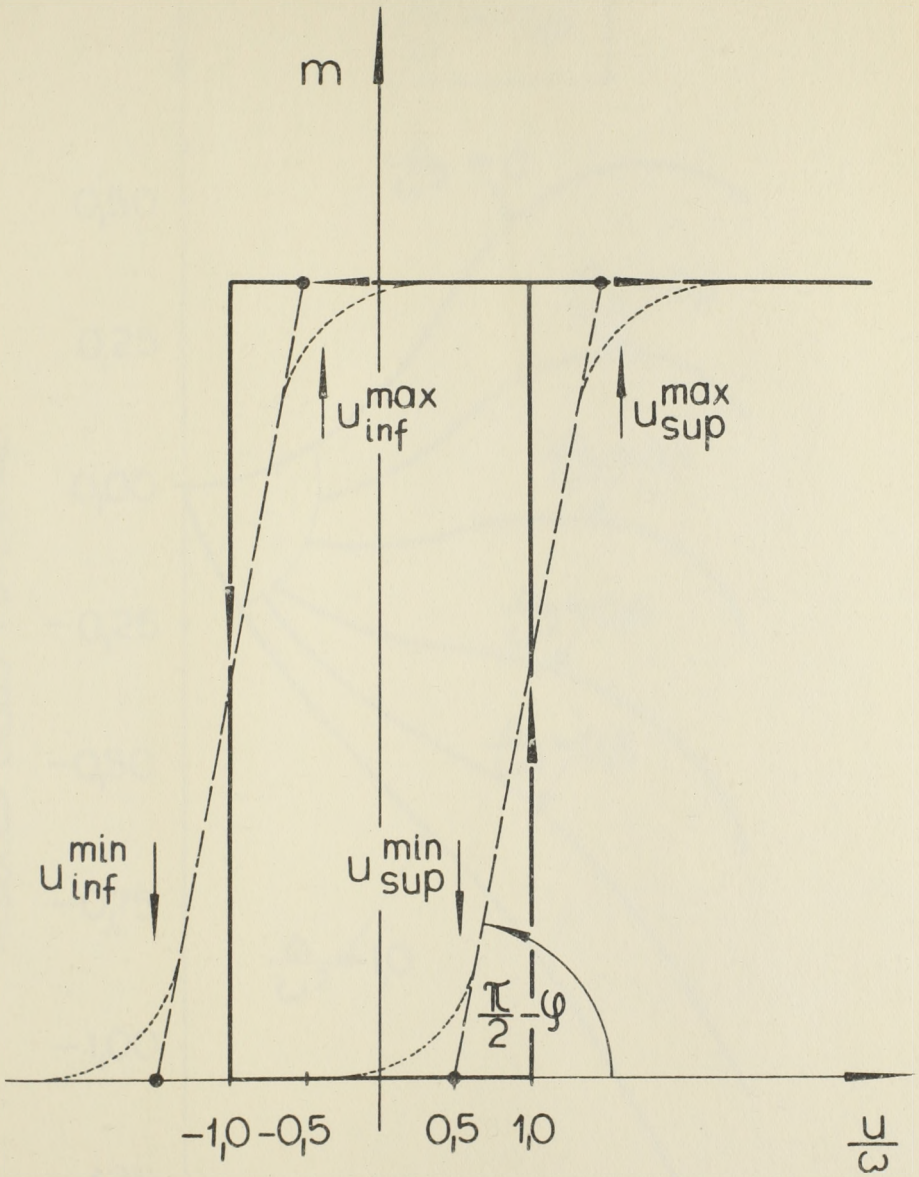

REDUCED GIBBS–POTENTIAL
1,00
0,75
0,50
0,25
0,00
−0,25
−0,50
−0,75
−1,00
0,00
0,25
0,50
0,75
1,00
m
PARAMETER OF BENDING
u/3 = −1,0
u/3 = −0,7
u/3 = −0,5
u/3 = 0,0
u/3 = 0,5
u/3 = 1,0

Fig. 4



TEMPERATURE PARAMETER

Fig. 5.

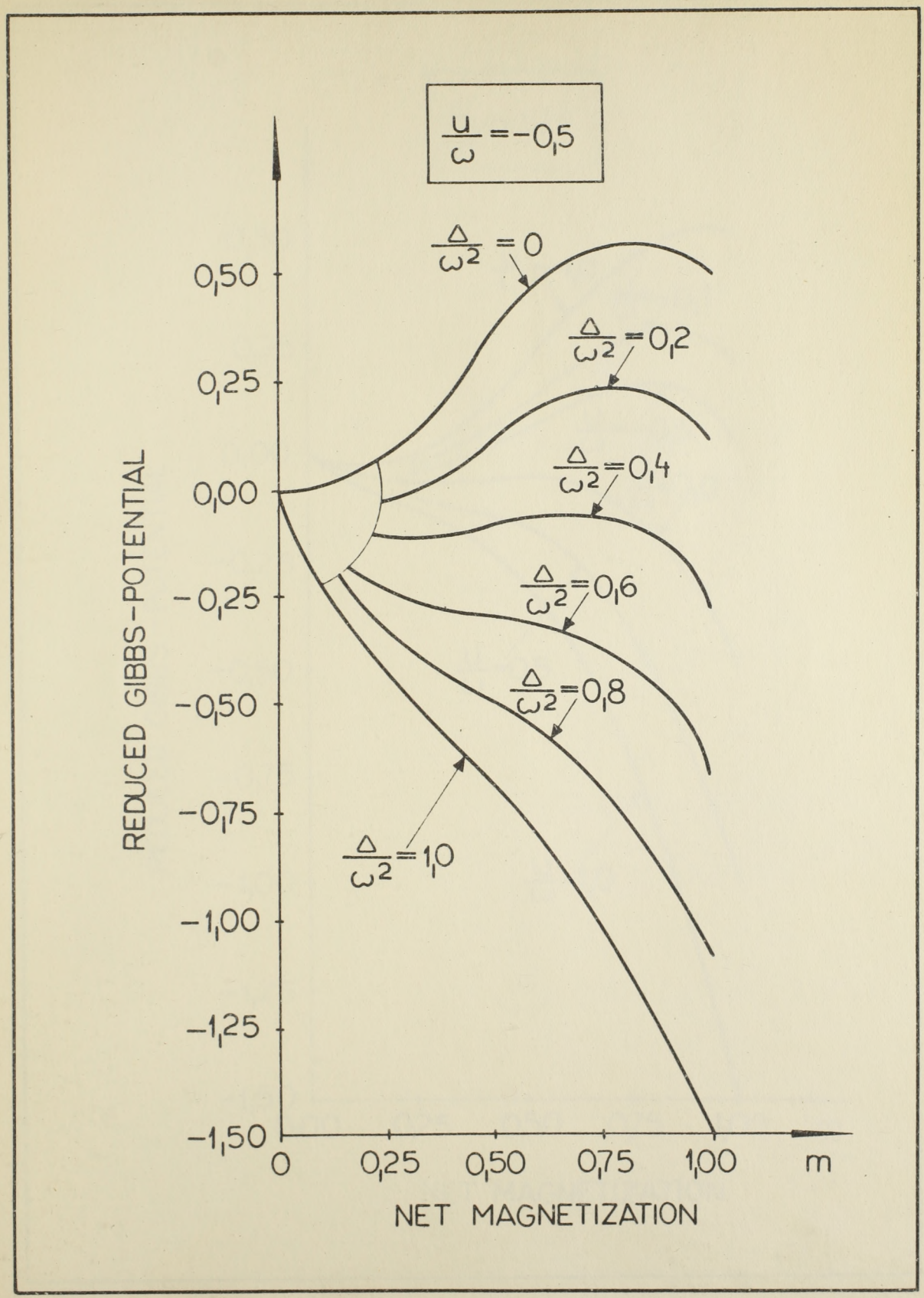

$\frac{u}{\omega} = -0{,}5$
$\frac{\Delta}{\omega^2} = 0$
$\frac{\Delta}{\omega^2} = 0{,}2$
$\frac{\Delta}{\omega^2} = 0{,}4$
$\frac{\Delta}{\omega^2} = 0{,}6$
$\frac{\Delta}{\omega^2} = 0{,}8$
$\frac{\Delta}{\omega^2} = 1{,}0$
REDUCED GIBBS-POTENTIAL
0,50
0,25
0,00
-0,25
-0,50
-0,75
-1,00
-1,25
-1,50
0
0,25
0,50
0,75
1,00
m
NET MAGNETIZATION

Fig. 6.

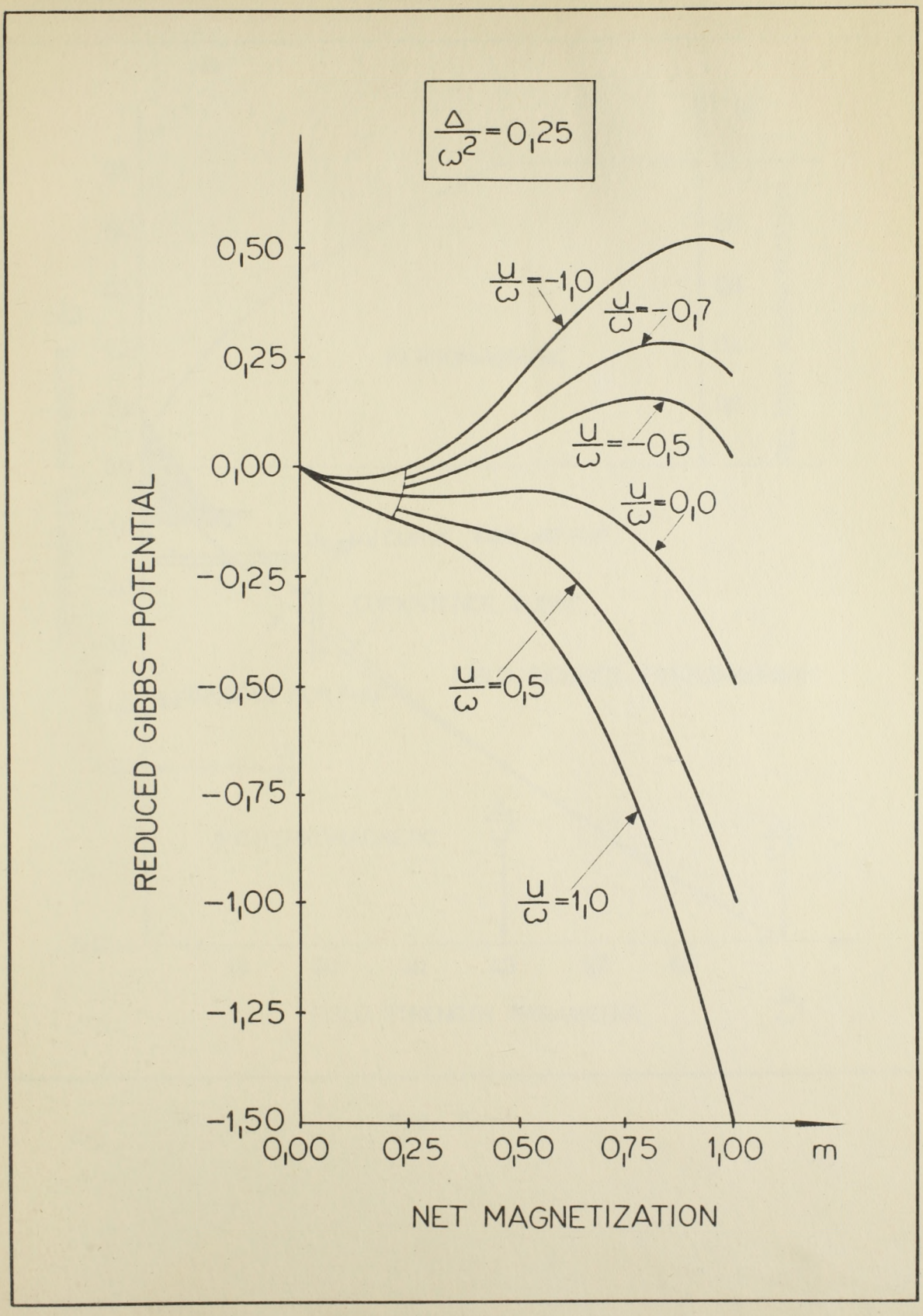

$\frac{\Delta}{\omega^2}=0,25$
0,50
0,25
0,00
-0,25
-0,50
-0,75
-1,00
-1,25
-1,50
$\frac{u}{\omega}=-1,0$
$\frac{u}{\omega}=-0,7$
$\frac{u}{\omega}=-0,5$
$\frac{u}{\omega}=0,0$
$\frac{u}{\omega}=0,5$
$\frac{u}{\omega}=1,0$
REDUCED GIBBS-POTENTIAL
0,00
0,25
0,50
0,75
1,00
m
NET MAGNETIZATION

Fig. 7

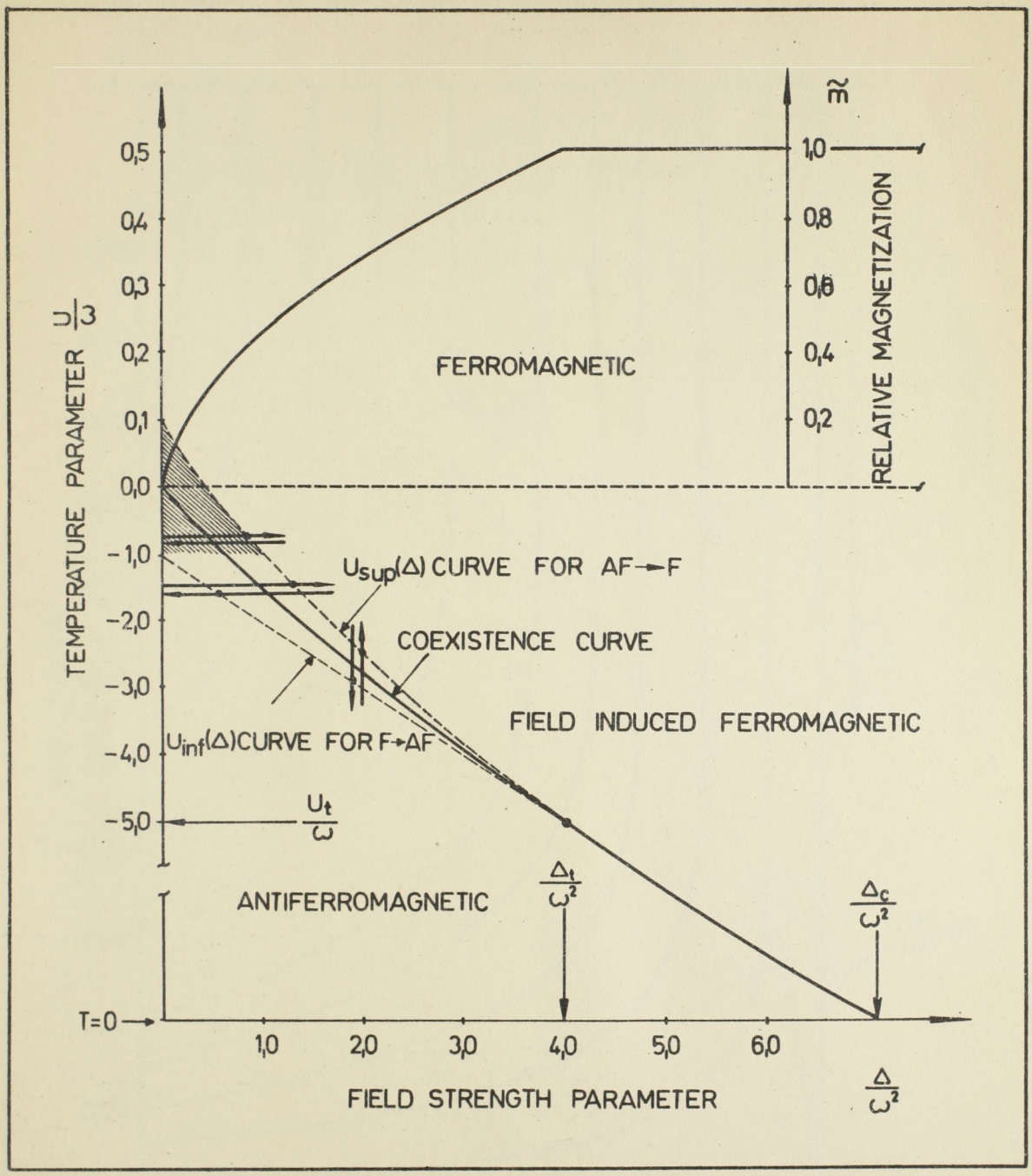

TEMPERATURE PARAMETER U/3
0,5
0,4
0,3
0,2
0,1
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
m
1,0
0,8
0,6
0,4
0,2
RELATIVE MAGNETIZATION
FERROMAGNETIC
U_sup(Δ) CURVE FOR AF→F
COEXISTENCE CURVE
FIELD INDUCED FERROMAGNETIC
U_inf(Δ) CURVE FOR F→AF
U_t/ω
ANTIFERROMAGNETIC
Δ_t/ω²
Δ_c/ω²
T=0
1,0
2,0
3,0
4,0
5,0
6,0
FIELD STRENGTH PARAMETER
Δ/ω²

Fig. 8.

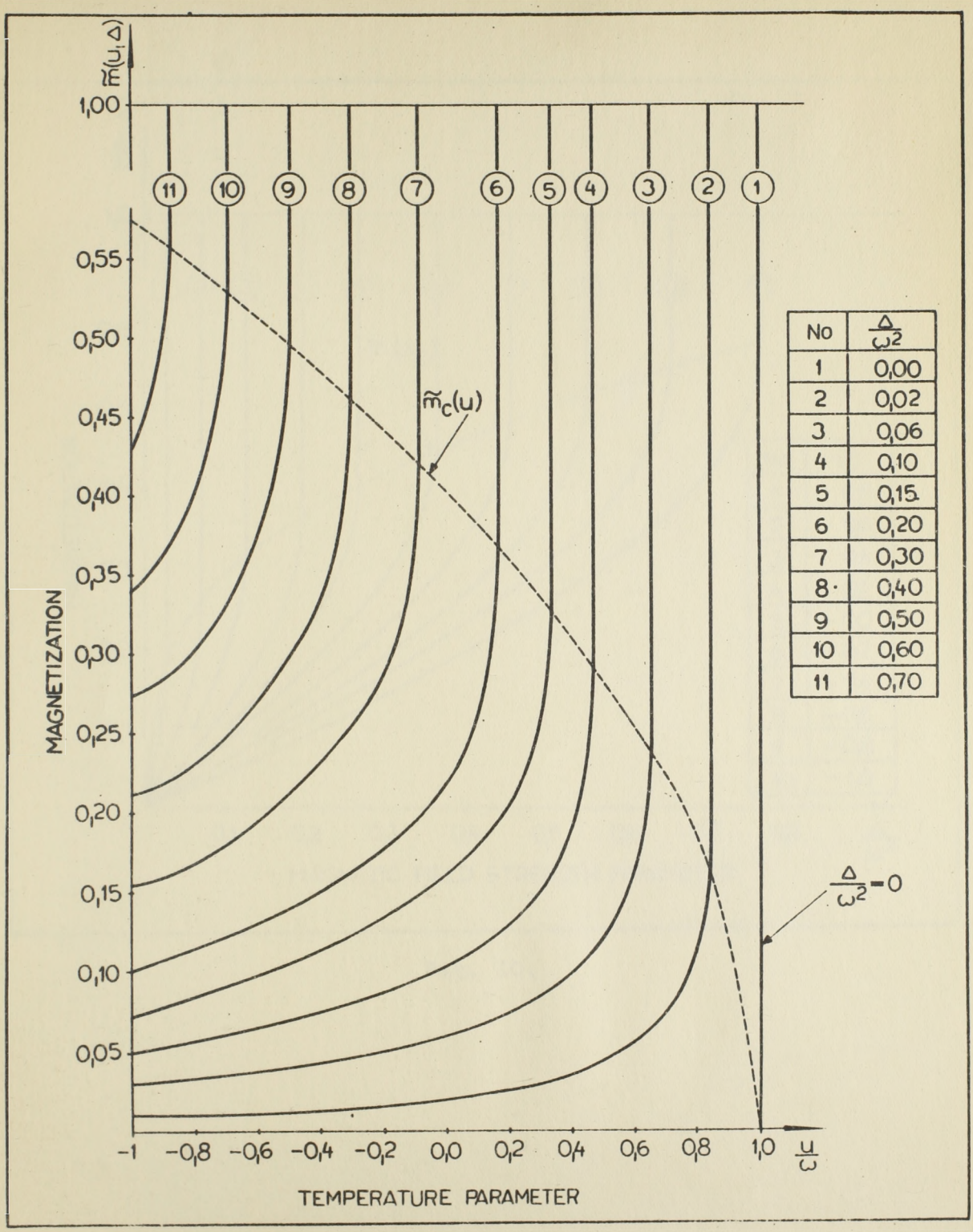

$\tilde{m}(u,\Delta)$
1,00
11
10
9
8
7
6
5
4
3
2
1
0,55
0,50
0,45
0,40
0,35
0,30
0,25
0,20
0,15
0,10
0,05
MAGNETIZATION
$\tilde{m}_c(u)$
$\frac{\Delta}{\omega^2}=0$
-1
-0,8
-0,6
-0,4
-0,2
0,0
0,2
0,4
0,6
0,8
1,0
$\frac{u}{\omega}$
TEMPERATURE PARAMETER
No
$\frac{\Delta}{\omega^2}$
1 0,00
2 0,02
3 0,06
4 0,10
5 0,15
6 0,20
7 0,30
8 0,40
9 0,50
10 0,60
11 0,70

Fig. 9

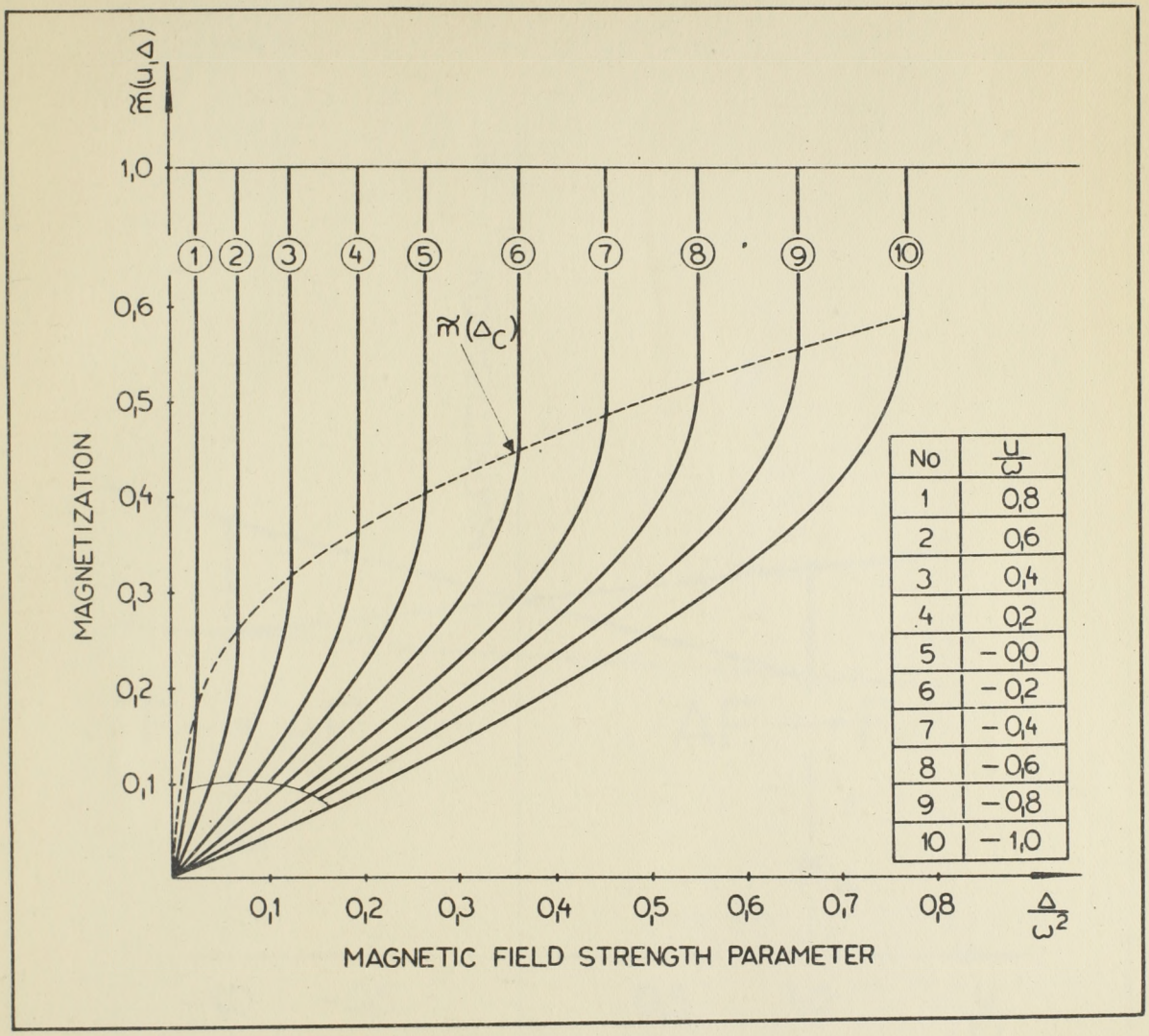
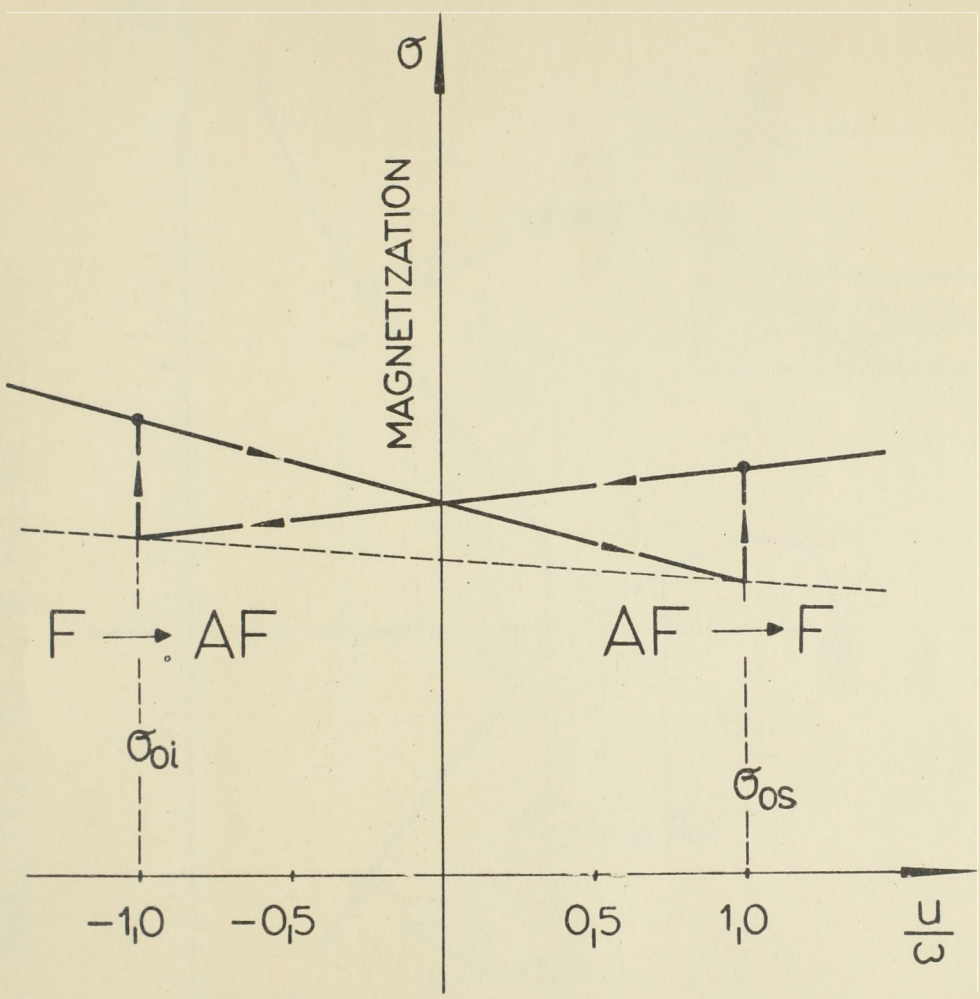

$\mathfrak{M}(u,\Delta)$
1,0
0,6
0,5
0,4
0,3
0,2
0,1
MAGNETIZATION
$\mathfrak{M}(\Delta_c)$
1 2 3 4 5 6 7 8 9 10
No | $\frac{u}{\omega}$
1 | 0,8
2 | 0,6
3 | 0,4
4 | 0,2
5 | −0,0
6 | −0,2
7 | −0,4
8 | −0,6
9 | −0,8
10 | −1,0
0,1 0,2 0,3 0,4 0,5 0,6 0,7 0,8
$\frac{\Delta}{\omega^2}$
MAGNETIC FIELD STRENGTH PARAMETER

Fig. 10.



TEMPERATURE PARAMETER

Fig. 11

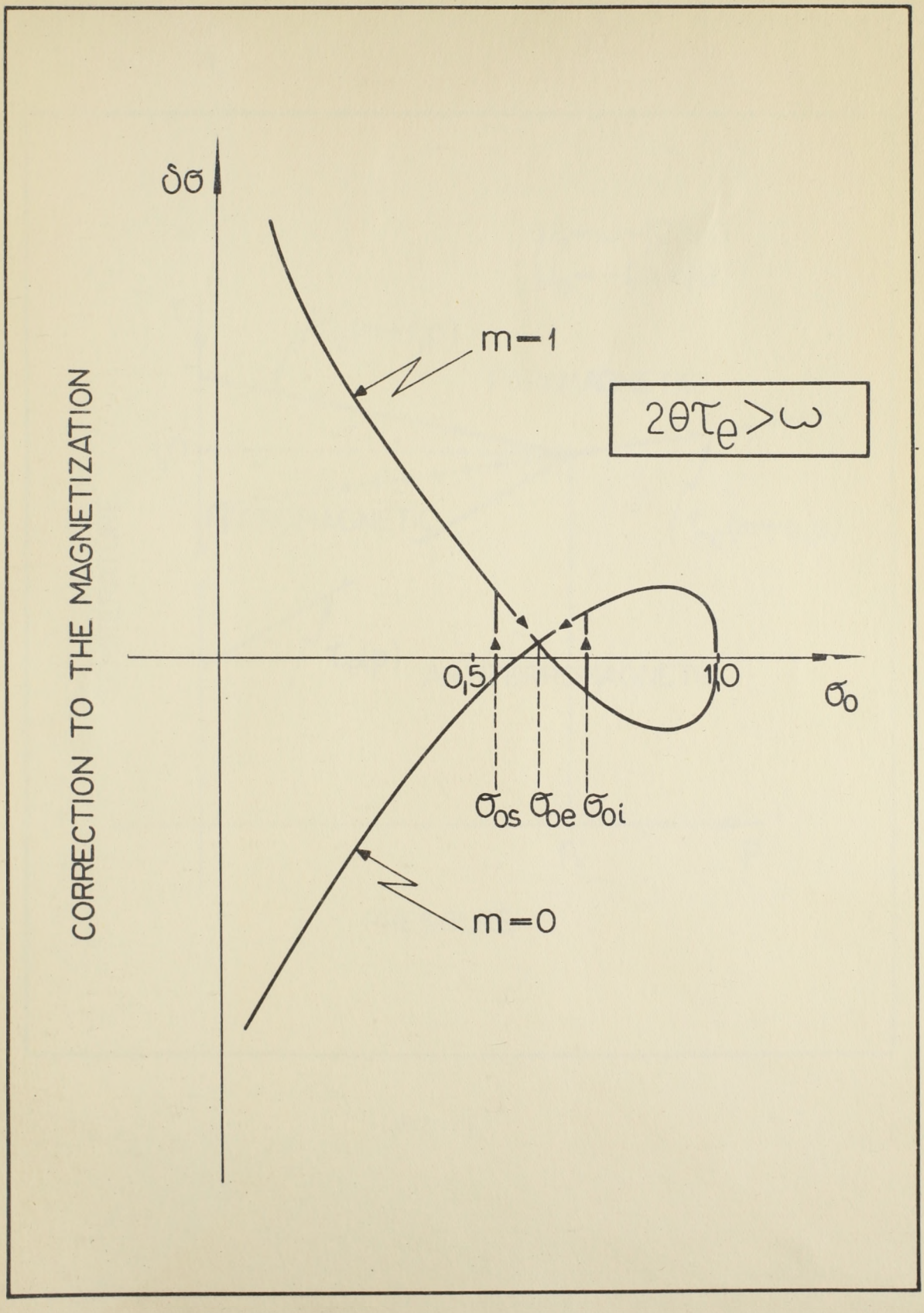

δσ
m=1
2θτe>ω
0,5
1,0
σ0
σ0s σ0e σ0i
m=0
CORRECTION TO THE MAGNETIZATION

Fig. 12

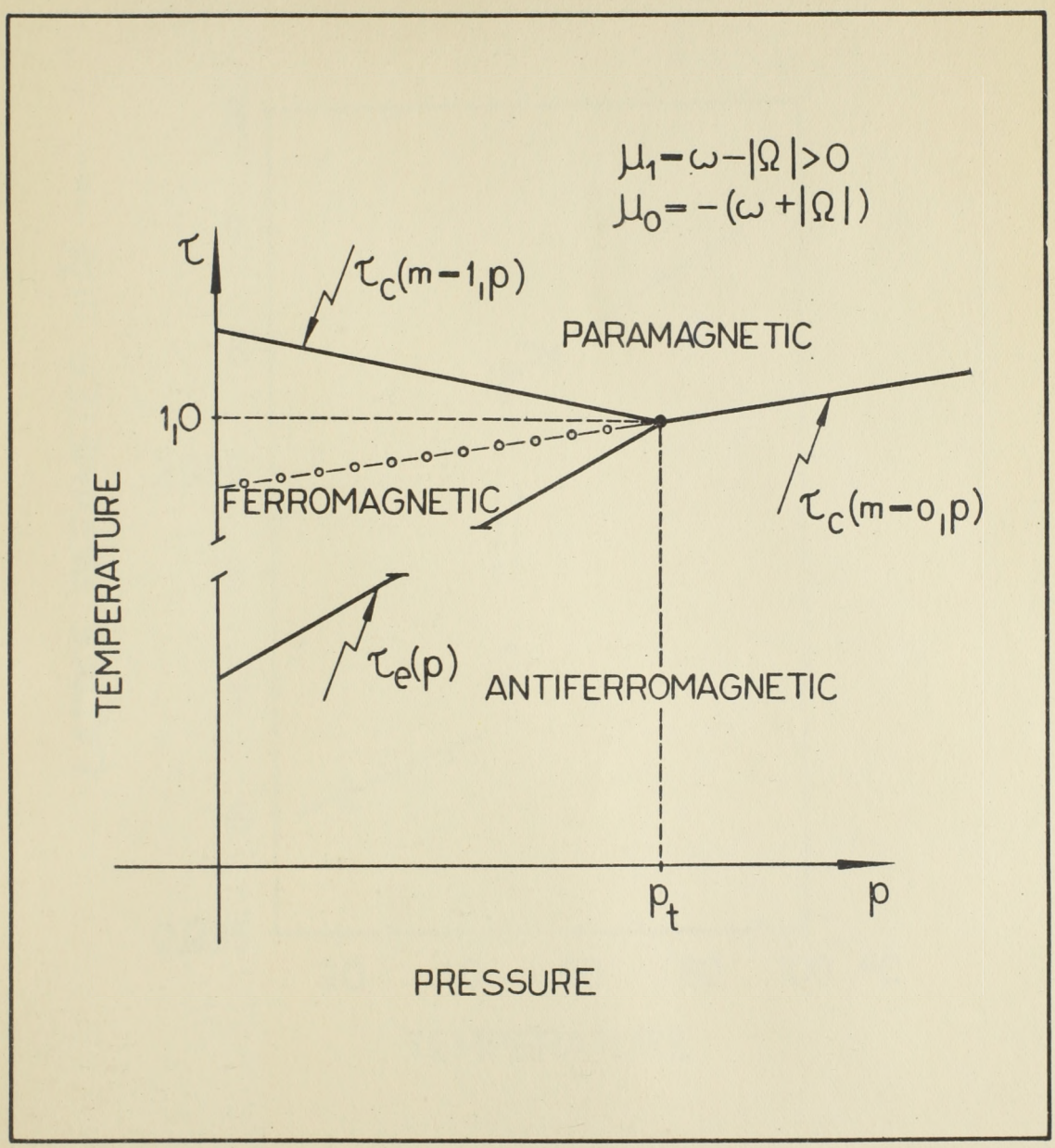

$\mu_1 = \omega - |\Omega| > 0$
$\mu_0 = -(\omega + |\Omega|)$
τ
$\tau_c(m=1,p)$
PARAMAGNETIC
1,0
FERROMAGNETIC
$\tau_c(m=0,p)$
TEMPERATURE
$\tau_e(p)$
ANTIFERROMAGNETIC
p_t
p
PRESSURE

Fig. 13

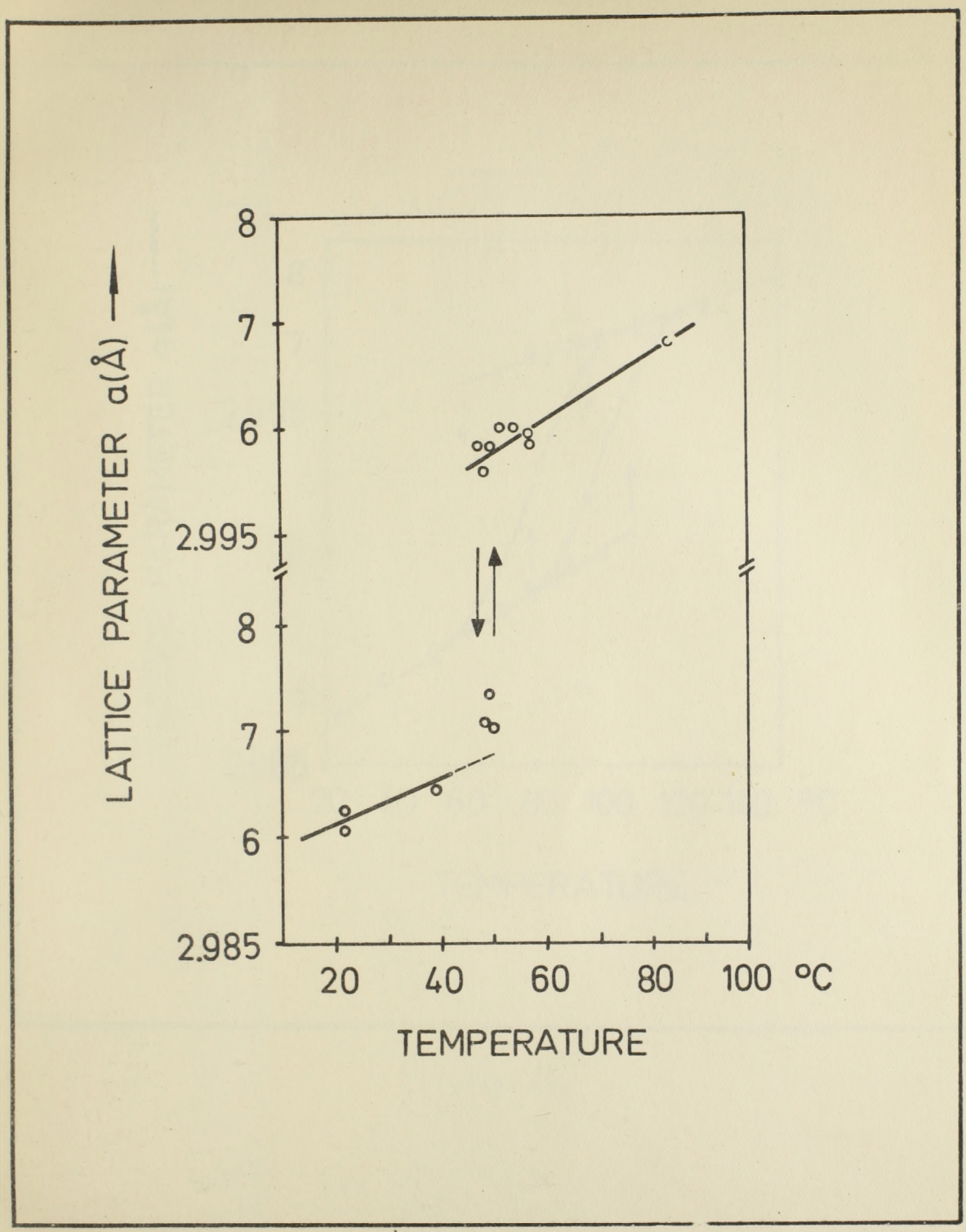

LATTICE PARAMETER a(Å)
8
7
6
2.995
8
7
6
2.985
20
40
60
80
100 °C
TEMPERATURE
c

Fig. 14.

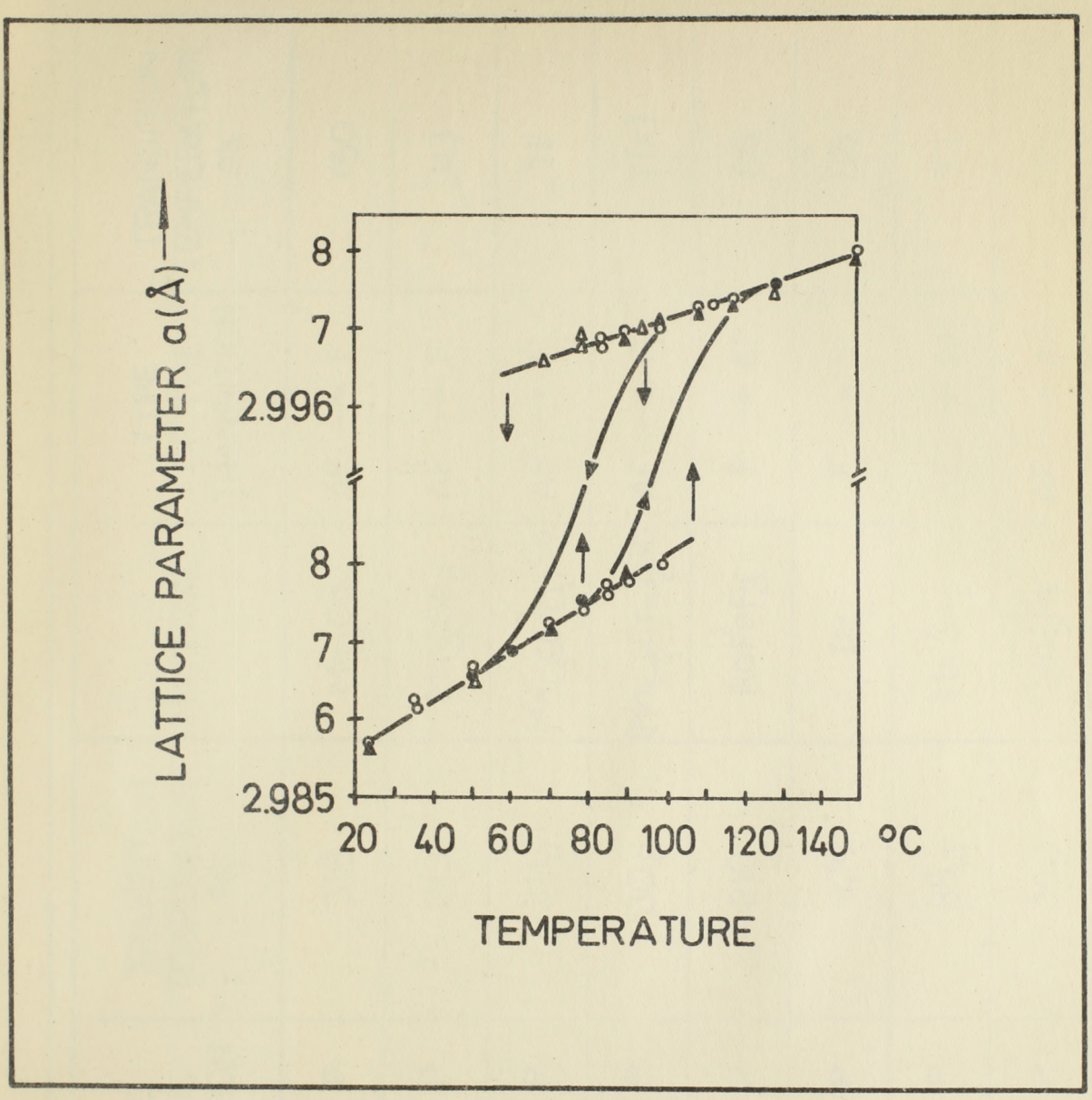

LATTICE PARAMETER a(Å)
8
7
2.996
8
7
6
2.985
20 40 60 80 100 120 140 °C
TEMPERATURE

Fig. 15.

MATERIAL	TYPE OF THE TRANSITION	TRANSITION TEMPERATURE °K	MATERIAL	TYPE OF THE TRANSITION	TRANSITION TEMPERATURE °K
MnAs	F → P	318	Mn_3GaC	AF → F	150
Cr_2As_2	F_i → P	213	Mn_3Ge_2	AF → F	113
Cr	AF → P	311_{17}	$Mn_{0,9}Li_{0,1}Se$	AF → F	71
UO_2	AF → P	30_{18}	$(Mn_{1-x}Cr_x)_2Sb$	AF → F_i	T(x)
$TiCl_3$	AF → P	210	$RbFeF_3$	F → AF	86
$MnBr_2$	AF → P	$2_{1}16$	Dy	F → S	85
$KMnF_3$	AF → P	88_{13}	$MnSn_2$	AF → AF	73
FeRh	AF → P	350	Mn_3Pt	AF → AF	365

Table I.

EIGEN–VALUE	EIGEN–VECTOR	STRUCTURE	INTERNAL ENERGY
$3(a+b)$	$\bar{M}_1=\bar{M}_2=\cdots\cdots\cdots=\bar{M}_8=\bar{M}$	FERROMAGNETIC F	$-12(a+b)M^2$
$-3(a-b)$	$\bar{M}_1=\bar{M}_3=\bar{M}_5=\bar{M}_7=\bar{M}$ $\bar{M}_2=\bar{M}_4=\bar{M}_6=\bar{M}_8=-\bar{M}$	ANTIFERROMAGNETIC AF I	$12(a+b)M^2$
$-(a+b)$	$\bar{M}_1=\bar{M}_3=\bar{M}_6=\bar{M}_8=\bar{M}$ $\bar{M}_2=\bar{M}_4=\bar{M}_5=\bar{M}_7=-\bar{M}$	ANTIFERROMAGNETIC AF II	$4(a+b)M^2$
$a-b$	$\bar{M}_1=\bar{M}_2=\bar{M}_3=\bar{M}_4=\bar{M}$ $\bar{M}_5=\bar{M}_6=\bar{M}_7=\bar{M}_8=-\bar{M}$	ANTIFERROMAGNETIC AF III	$-4(a-b)M^2$

Table II.

	F ⇄ AFI	AFI ⇄ AFII	AFII ⇄ AFIII	AFIII ⇄ F
A	$6N\mathcal{J}_2$	$-\frac{3}{2}N\mathcal{J}_1$	$-2N\mathcal{J}_2$	$\frac{3}{2}N\mathcal{J}_1$
B	$3N\mathcal{J}_1$	$N(4\mathcal{J}_2-\mathcal{J}_1)$	$-N\mathcal{J}_1$	$-N(4\mathcal{J}_2-\mathcal{J}_1)$
γ	0	$\frac{1}{2}$	0	$\frac{1}{2}$

Table III.

$m=1$	$\left(\frac{d\delta\sigma}{d\sigma_0}\right)_{\sigma_0=1}$		$\delta\sigma(\sigma_0)=0$		$\delta\sigma(\sigma_0=0)$
	$2\theta\tau_e>\omega$	$2\theta\tau_e<\omega$	$2\theta\tau_e>\omega$	$2\theta\tau_e<\omega$	
$\mu_1>0$	$+\infty$	$-\infty$	yes	no	$+\infty$
$\mu_1<0$	$-\infty$	$+\infty$	yes	no	$-\infty$

$m=0$	$\left(\frac{d\delta\sigma}{d\sigma_0}\right)_{\sigma_0=1}$	$\delta\sigma(\sigma_0)=0$	$\delta\sigma(\sigma_0=0)$
$\mu_0>0$	$+\infty$	yes	$+\infty$
$\mu_0<0$	$-\infty$	yes	$-\infty$

Table IV.